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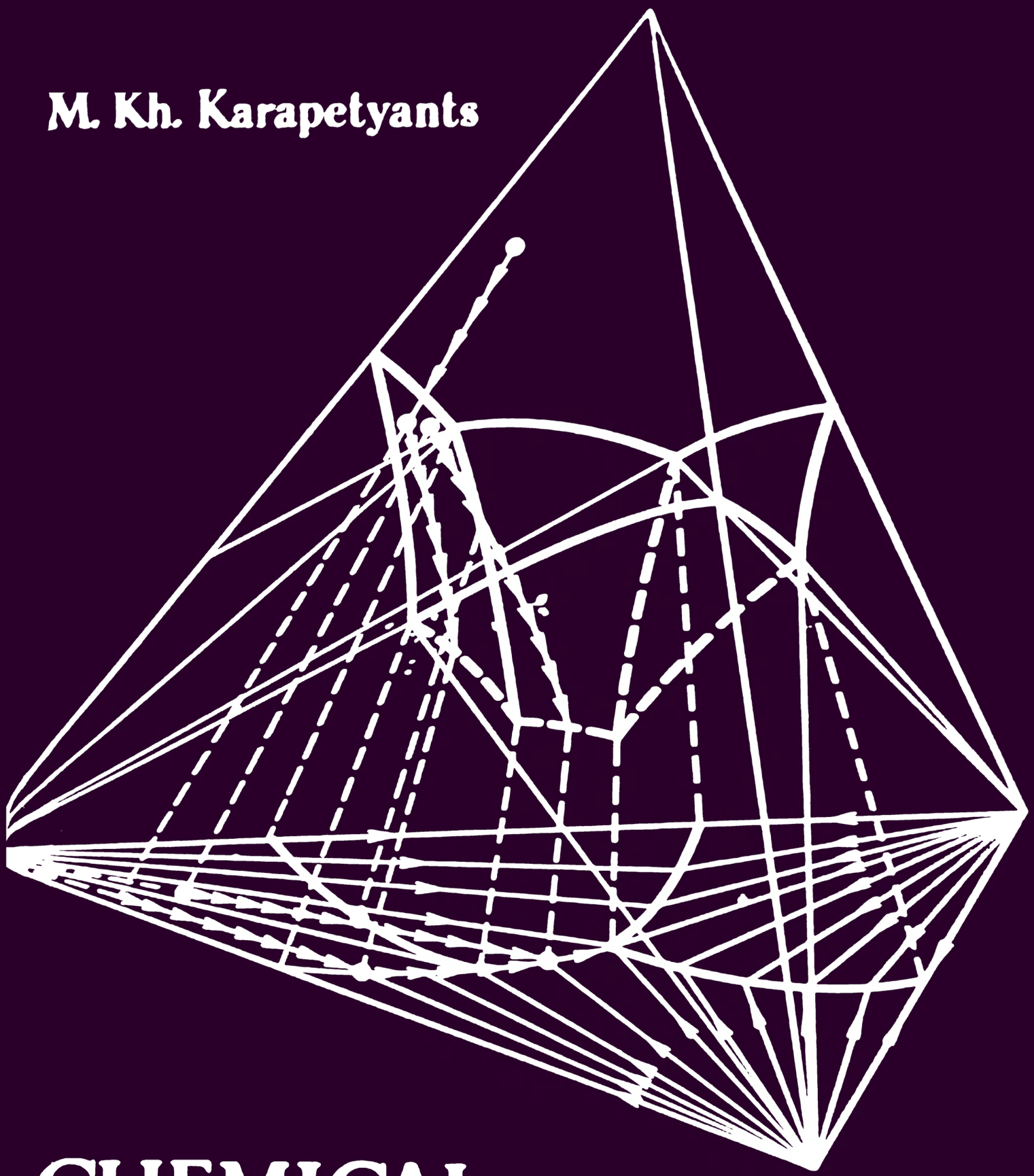

CHEMICAL THERMODYNAMICS

MIR PUBLISHERS

M. Kh. Karapetyants

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М. Х. КАРАПЕТЬЯНЦ

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Preface

The present book is intended mainly for students of higher educational establishments specializing in chemistry, and primarily for future engineers. This is why I have tried to avoid abstractness and needless theorization, which could keep the essence of the material and its practical significance concealed behind a veil of formal mathematical calculations and abundant formulas and equations. This naturally does not mean that the course ought to be reduced to a set of recipes, because such an approach cannot create a firm theoretical foundation and will not make the reader understand the great variety of practical problems.

Most thermodynamic relationships have no practical value, because they contain quantities, part of which are either unknown or can be calculated only roughly. Hence, solving a specific problem with even an approximate assessment of the numerical value of the needed quantity is frequently impossible. Therefore, while rendering my due to theory, I also give various approximate laws that make it possible to rapidly obtain the required results and predict unavailable data with an accuracy sufficient for practical purposes.

My experience in teaching physical chemistry and chemical thermodynamics convinced me that "chemization" facilitates the mastering and successful application of these courses. This prompted me to combine the introduction of elements of "empirical thermodynamics" with a depiction of the relationship between thermodynamic properties on one hand and the nature of a substance and Mendeleev's Periodic Table on the other. The limited size of the book did not permit the latter to be done entirely. It was done most completely only for entropy, whose meaning students usually find the most difficult to understand.

On the other hand, many years of lecturing on general and inorganic chemistry convinced me of the need to "thermodynamize" it. This not only improves its scientific level, but also prepares the students for comprehending the material of subsequent courses,

especially physical chemistry and chemical thermodynamics, thus raising the level of teaching of the fundamental branches of chemistry as a whole and ensuring their continuity. I also attempted to do this in my book "An Introduction to the Theory of Chemical Processes" [M. Kh. Karapetyants. *Vvedenie v teoriyu khimicheskikh protsessov*, 2nd ed. Moscow, Vysshaya shkola (1975) *].

In treating the material, I give primary attention to the thermodynamics of gaseous systems while the thermodynamics of solutions is dealt with less completely, and still less space is devoted to solutions of electrolytes.

The fruitful mastering of thermodynamics in general, especially for a technologist, is conceivable only when the student sees how theory is applied to the solution of various practical problems. This is why the present volume contains many examples designed to help the student consolidate the theoretical information and acquire competence in calculations. The majority of the examples are connected with the technology of inorganic substances and of the chemical processing of fuel. The calculations have been selected as far as possible so that the results obtained can be compared with experimental data.

Most graphs have been plotted using concrete data. This should not only facilitate the understanding of the corresponding hypotheses, laws and equations, but also allow them to be used in calculations, which, in turn, should facilitate a mastery of the material.

Almost all the examples and figures have been compiled on the basis of material taken from reference books and articles in various journals (only a few were taken from monographs, textbooks and problem books).

The book has many tables containing the most important characteristics of various substances and processes. These data are given not so much to show the scale of the relevant quantities and to illustrate various relationships, as to use them in various calculations.

The bibliography at the end of the book covers training aids, monographs, problem books and reference books. References to some sources are given directly in the text.

I find great pleasure in expressing gratitude to my wife Mariya L. Karapetyants, Cand.Sc., for her great assistance in preparing the manuscript.

M. Kh. Karapetyants

* See also M. Kh. Karapetyants. In : *Sbornik nauchno-metodicheskikh statei po khimii* (A Collection of Scientific and Methodological Articles on Chemistry). Moscow, Vysshaya shkola, Vyp. 2 (1970), 3 (1974), 4 (1975) and 6 (1977).

Chapter 1

INTRODUCTION

1.1. THE SUBJECT AND METHOD OF THERMODYNAMICS

Physical and chemical phenomena in thermodynamics are mainly investigated with the aid of two fundamental laws called the **first and second laws of thermodynamics.** The former follows from the law of conservation of energy and matter. The second law characterizes the direction of processes and was formulated in the 19th century. The present century saw the discovery of the **third law of thermodynamics,** which is not as broad and universal as the first and second laws, but is of great importance for the theoretical analysis of chemical processes.

Classical (phenomenological) thermodynamics embraces a complex of laws derived mathematically from the logical development of the above laws of thermodynamics. It is constructed according to a purely deductive principle: the laws of thermodynamics are considered as experimental generalizations, and corollaries for different particular cases are derived from them.

Thermodynamics is a science of macrosystems. It does not deal with separate particles (molecules, atoms, electrons and the like) or a small number of them. The state of the objects considered in thermodynamics is determined by directly measured quantities characterizing substances. The structure of a substance and the mechanism of a process are not considered.

The merging of certain branches of thermodynamics and statistical mechanics led to the appearance of **statistical thermodynamics.** The latter helped scientists to determine the physical meaning of the quantities contained in thermodynamic equations and find the absolute values of quantities for which thermodynamics gives only relative values. The statistical method is very fruitful in considering the second law and in calculating chemical equilibria.

Thermodynamics makes it possible to determine *a priori* whether or not a process is in principle possible and thus avoid experiments destined to be unsuccessful. Thermodynamic analysis, however, by determining the "motive power" of a process, permits us to indicate only its direction. To find the rate of a process, we must

know its resistance. The determination of the latter is connected with consideration of the mechanism of the process, but the latter is not studied by thermodynamics. Consequently, the thermodynamic method cannot be used in studying such phenomena as diffusion and heat transfer.*

The historically formed name of our subject does not correspond to its content. No "motion of heat" is dealt with in thermodynamics, and for this reason the similarity of the terms "thermodynamics" and "hydrodynamics" ("aerodynamics") is only linguistic.

It is customary to distinguish general (or physical), technical and chemical thermodynamics.

General thermodynamics sets out the theoretical fundamentals of thermodynamics, its laws and their application mainly to physical phenomena (to the properties of solids, liquids and gases, to electrical and magnetic phenomena, radiation, etc.).

Technical thermodynamics deals with the basic laws as applied to the processes of the mutual conversion of heat and work. Its main object is the development of the theory of heat engines to ensure their rational design and operation.

Chemical thermodynamics studies the application of the laws of thermodynamics to chemical and physicochemical phenomena. It mainly considers:

(1) the heat balances of processes, including the heat effects of physical and chemical processes;

(2) phase equilibria for individual substances and mixtures;

(3) chemical equilibrium.

Heat balances are compiled on the basis of the first law of thermodynamics. Phase and chemical equilibria are analysed on the basis of the second and third laws.

The studying of the laws describing chemical and physical equilibria is particularly important in chemical thermodynamics. A knowledge of them makes it possible to solve a multitude of very important problems encountered in production, design and research without resorting to experiments. The chief objectives here are as follows:

(1) determining the conditions in which a given process becomes possible (without performing work from outside);

(2) finding the limits of stability of a substance (or group of substances) being studied in a definite set of conditions;

(3) determining how to reduce the amount of undesirable substances produced in a reaction or even completely prevent their formation, i.e. how to suppress or eliminate secondary reactions;

* The last few decades have seen the development of the thermodynamics of irreversible processes, which analyses the course of various processes in time (see [B11, 13, 14, 34, 53, 82, 105]).

(4) selecting the optimal conditions of a process (the temperature, pressure, concentration of the reactants), etc.

Experiments are needed only to find the conditions favouring the course of a process at a sufficient rate (assuming thermodynamic calculations indicate that the reaction is in principle possible).

The following two examples can illustrate the significance of thermodynamics in chemistry.

1. The reduction of iron oxide in the blast-furnace process can be described by the following summary equation:

$$Fe_3O_4 + 4CO = 3Fe + 4CO_2\uparrow$$

The flue gases contain much carbon monoxide. Deciding that the cause of incomplete reduction was the insufficient time of contact of the coal with the ore, iron manufacturers began to build higher furnaces in the 19th century. Enormous sums of money were spent to no avail: the content of CO hardly diminished. Thermodynamic calculations later established that this reaction can proceed in a blast furnace only up to a definite limit and that a considerable content of carbon monoxide is inevitable.

2. At the end of the 19th century, attempts were made to prepare diamonds from graphite, but they were not successful. After the properties of these two modifications of carbon had been determined, it was found that the attempts to prepare diamonds were made in conditions in which graphite is more stable.

1.2. BASIC CONCEPTS AND DEFINITIONS

1.2.1. Systems and Their Classification

Thermodynamic analysis is preceded by separating out a complex of bodies being considered, called a **system.** It is usually limited by physical, i.e. natural, boundaries; it is sometimes convenient to artificially confine a system by means of arbitrary imaginary surfaces. The remaining part of space forms the **surroundings.**

A complex of bodies that can exchange energy or substances, or both, between one another and with other bodies is called a **thermodynamic system.** The interaction of a thermodynamic system (in the following we shall call it simply a system) and the surroundings is connected with the transfer of heat and the performance of work.

A thermodynamic system that does not exchange energy and a substance with other systems is called **isolated.**

Any system is characterized by a definite state; if it does not change in time, i.e. if there are no flows of substance and energy in the system and its invariability is not due to any external processes, then the system is in the **equilibrium state.**

A system is **heterogeneous** if it consists of parts differing in properties and separated by interfaces. A system having no interfaces is called **homogeneous.** Homogeneous systems are uniform, but sometimes depart from this property due to a continuous (from point to point) change in their properties within their entire volume (for instance a column of air).

A complex of parts of a heterogeneous system separated by interfaces and characterized in the absence of an external field of forces by identical physical properties at all its points is called a **phase.**

1.2.2. Thermodynamic Parameters

The state of a thermodynamic system is characterized by an aggregate of quantities called **thermodynamic parameters.** Any property of a system can be a thermodynamic parameter if it is considered as one of the independent variables determining the state of the system. Properties of a system may be **extensive** if they depend on the amount of substance, for example volume, and **intensive** if they do not depend on its amount, for example temperature, molar (specific) volume and concentration. The value of an extensive property is equal to the sum of the values of this property for separate parts of a system.

The parameters of state lending themselves to direct measurement are customarily considered as the basic ones. They include temperature, pressure, density, molar (specific) volume and concentration. The internal energy, enthalpy, entropy and other parameters are usually considered as functions of the basic parameters. Other properties are studied only in special cases. For example, the refractive index is considered in the thermodynamics of optical phenomena.

It is important to emphasize that the thermodynamic parameters of state of a system characterize only its *given* state, and are not witnesses of its preceding states. *When a system transfers from one state to another, the change in its properties does not depend on the path of the transition (process), but is determined only by its initial and final states,* i.e. by the thermodynamic parameters in these two states. In particular, if a system after departing from a certain initial state and undergoing a number of changes returns to the initial state, i.e. completes a **cyclic process (cycle),** then at the end of the process it acquires the same properties which it had in the initial state. We can thus ignore the nature of a process and characterize the change in a system by considering only its initial and final states.

The fact that a change in the properties of a system is independent of the transition path is not confirmed in practice when the rate of

change in the state of a system is less than that of the change in its surroundings. Such phenomena are observed for liquids only at very low temperatures, but are characteristic of solids owing to their slow rate of structural transformations caused by a change in the surroundings. For this reason, a solid which after passing through different processes returns to the same conditions (for example to the initial ones) may have different properties. Thus, rapid cooling of an alloy (hardening) makes it possible to keep it in the state corresponding to high-temperature equilibrium, while subsequent heating facilitates the transition to a stable state. By changing the rate of cooling and subsequent heating, as well as the duration of holding the alloy at different temperatures, we can obtain alloys with a variety of properties more or less approaching the equilibrium structure. For example, by subjecting hardened steel to heat treatment, we can bring it partly (by tempering) or completely (by annealing) to a thermodynamically stable state.

Although we quite often have to deal with systems that are in a state of retarded equilibrium (such systems include silicates, whose high viscosity prevents the achievement of equilibrium), this does not affect the correctness of the results of thermodynamic calculations. It is always possible to imagine an insignificant rate of change in the surroundings such that the state of a system at each moment will correspond to them.

Technical thermodynamics, being concerned with an analysis of the operation of various machines, deals with cyclic processes. For this reason a study of the subject should be based on the **method of cycles.** Chemical thermodynamics can use a different method. We know that in chemistry and chemical engineering, processes are conducted which result in a system passing from one state to another differing from the initial state. With respect to the *practical* application of a chemical process, the principle of a cycle is not rational. This is why the **method of functions** is also frequently used. This method is based on the change in the properties of a system being independent of the nature of a process and, moreover, is simpler than the method of cycles. The method of functions can be used to consider many complicated problems whose solution by the method of cycles is much more difficult and sometimes results in cumbersome operations.

Pressure and Temperature. **Pressure** characterizes the interaction of a system with its surroundings. This is a parameter of state which is determined by the force acting in a body per unit of its surface area along a normal to it. If a system is in equilibrium, the pressure is identical in all its parts and is equal to the external pressure.

By contrast, **temperature,** which determines a measure of the intensity of thermal motion of the molecules, cannot be expressed in simple quantities. First, the concept of a temperature *difference* is established, which shows how far a body deviates from thermal equilibrium with another body at the same pressure. When bodies having different temperatures come into contact, the temperatures level out as a result of heat passing from the hotter body to the colder one — the system passes over to a state of thermal equilibrium.

Any property of a substance whose change is connected with a change in temperature (volume, electrical resistance, thermoelectromotive force, etc.) may serve for the quantitative determination of the temperature. Most often a change in volume (length) is used when measuring the temperature. The thermometric substance is brought into contact with water, which is usually chosen as the standard or reference substance. The volumes of the thermometric substance corresponding to two easily reproducible values of the temperature — the melting point of ice and the boiling point of water — are measured. The difference between the two volumes is divided into an equal number of parts (for example into 100 parts). In this way an **empirical scale** of temperatures is obtained.

Generally speaking, the value of a degree of temperature and the beginning of its scale are *arbitrary*. Any substance could be used as the reference one instead of water (if only its properties changed unambiguously with the temperature, were reproducible and easily lent themselves to measurement); other states of the reference substance could have been chosen and the difference between the volumes of the thermometric substance divided into a different number of parts.

Such an arbitrary nature of the selection disappears if we use the so-called **thermodynamic (absolute) scale** of temperatures based on the second law of thermodynamics (see Chap. 4). The initial point of this *universal* scale is the value of the lowest possible temperature — **absolute zero,** equal to —273.15 °C. Readings on the absolute scale coincide with the temperature measured using a thermometer filled with a gas at a negligibly low pressure (theoretically an ideal gas).

With the introduction of the absolute scale, the measurement of temperature and the very notion of it are relieved of the individual features of the thermometric substance. The relationship between the properties of substances is now expressed in the simplest possible manner.

Equation of State. The properties whose complex is determined by the state of a system are related to one another: a change in one of them is attended by a change in at least one other. This

mutual relationship is expressed by a functional dependence of thermodynamic parameters. An equation relating the thermodynamic parameters of a system in the equilibrium state is called an **equation of state.** Thus, the equation $\varphi(p, V, T) = 0$ is an equation of state for a pure substance if an electrical and a magnetic fields are absent, the gravitational and surface energies are neglected, the volume is uniformly filled, and the pressure and temperature are constant in all parts of the system. Still another condition appears for a homogeneous mixture (solution) : the constancy of the concentration of the substances throughout the entire volume. When dealing with a heterogeneous system, each phase will be characterized by its own equation of state.

In the relatively rare cases of processes in surface layers, we must introduce a new quantity — the **surface energy.** For example, to determine the state of a drop of liquid in equilibrium with its vapour, we must also take into account the curvature of the surface (see Sec. 7.6), since in this case the surface energy is relatively great (if the drop also carries an electric charge, a new variable will appear, and the pressure of the saturated vapour will change). In general, the influence of the particle size should be taken into consideration when studying various properties of highly dispersed systems. Thus, the heat capacity of very fine (about 200 Å) crystals of MgO is 7% greater than that of large crystals.

If any state complying with the above conditions can be expressed by an equation of state, then the reverse conclusion does not hold. For instance, we can indicate the values of p, V and T satisfying the equation of state $\varphi(p, V, T) = 0$, but not corresponding to any physically possible states. An example is the state corresponding to any point on any of the van der Waals isotherms below the critical temperature and to the section of the curve on which $(\partial p/\partial V)_T > 0$ (see p. 94).

Owing to the mutual relationship between the properties of a system, it is sufficient to indicate only a certain number of its properties in order to determine its state. Thus, the state of a gas can be considered as given if two parameters are indicated, for example temperature and pressure. The value of volume will be determined from the equation of state $V = \varphi(p, T)$.

Graphically, the equation $\varphi(p, V, T) = 0$ is the equation of a surface plotted on three mutually perpendicular axes, each of which corresponds to one thermodynamic parameter. Consequently, any equilibrium state of a system, determined by a certain complex of numerical values of the parameters, will be depicted by a point lying on the thermodynamic surface obtained. Such a point is called **figurative**, and the surface, **characteristic.** When the state

of the system changes, the figurative point moves along the surface, describing a certain curve.

Thus, a **thermodynamic surface** is the locus of points depicting the equilibrium states of the system in functions of the thermodynamic parameters.

1.2.3. Work and Heat

Work and heat are quantitative characteristics of two forms of the *exchange* of energy between a system and its surroundings. The **work of a process** is the energy transmitted by one body to another upon their interaction; it does not depend on the temperature of the bodies and is not connected with the transfer of matter from one body to another.

The **work** (W) done by a system is due to *interaction* between the system and the surroundings as a result of which the external forces violating equilibrium in the system are overcome. Work is determined by the sum of the products of the forces *acting on a system* and the corresponding distance (the products of the pressure and the change in volume, the surface tension and the change in surface area, etc.). If the *external* pressure is the only force acting on a system, then the polynomial expressing the work transforms into a monomial. This term acquires the form $p\,dV$ for an elementary process during which the external pressure can be considered constant. Unless otherwise indicated, we shall deal with systems subjected only to the action of pressure, and shall hardly ever treat cases when the work cannot be expressed by $\int p\,dV$.

In thermodynamics, the work done by a system on its surroundings (for example, in the expansion of a gas, vaporization, dissociation) is considered to be positive. When work is performed by external forces (for example, in the compression of a gas), it is considered to be negative.

The energy transmitted by one body to another when they interact dependent only on their temperatures and not connected with the transfer of matter from one body to the other is called the **heat of a process.** The liberation or absorption of heat (Q) by the system is the result of the violation of thermal equilibrium between the system and its surroundings. In thermodynamics, the heat supplied to a system is considered positive, and that given up by it — negative. Thus, the heat effect of an exothermic chemical reaction is negative, and that of an endothermic one is positive. A process in which a system neither receives nor returns heat to its surroundings is called **adiabatic.**

1.2.4. Reversible and Irreversible Processes

Any change in a system connected with a change in at least one thermodynamic parameter is called a **thermodynamic process.**

Assume that a system in a state of thermodynamic equilibrium is subjected to continuous infinitely small actions by the surroundings as a result of which it passes through a *consecutive series of equilibrium states.* If the maximum possible work is done in this case, then an **equilibrium process** occurs in the system.

It can be seen from the definition that an equilibrium process has the following features.

1. A two-directional nature (since the direction of the process is determined by an infinitely small action on the system).

2. The absence of any losses (since the system does the maximum possible work).

3. Equality of the forces acting on the system (pressure, electric field, etc., depending on the nature of the process) to the forces counteracting them from the system (more precisely, an infinitely small difference between their values). Only upon the equilibrium expansion of a gas may we use the equation

$$W = \int_1^2 p\, dV$$

where p is the pressure in the system.

Therefore, only upon the equilibrium expansion of an ideal gas for one mole of which we have $pV = RT$ does the work equal

$$W = \int_1^2 p\, dV = \int_1^2 \frac{RT}{V} dV$$

In non-equilibrium expansion

$$W < \int_1^2 \frac{RT}{V} dV$$

4. Equality between the temperatures of the system and the surroundings (more precisely, an infinitely small difference between them) if the system is not isolated by means of an adiabatic shell.

5. An infinitely great duration of the process for any finite change in the state of the system. This feature is due to the infinitely low

rate of the process. Indeed, if the rates are finite, an infinitely small change in the acting force will not be sufficient for the process to occur. This is explained by the appearance of finite differences in the quantities p and T both in the system itself and between it and the surroundings, and by the appearance of losses, for instance due to friction. Thus, although this feature is not significant in thermodynamics (since the duration of a process is not considered), it has great practical importance.

If an equilibrium process takes place at an infinitely slow rate, this by no means indicates that the reverse statement holds in the general case. For instance, the discharge of a capacitor through a very great resistance proceeds very slowly, but is not an equilibrium process. The opposite cases are possible when a process occurs at a finite rate, but is an equilibrium one (rapid processes under conditions when frictional forces are practically absent). Both cases, however, are rare exceptions to the rule. A process involving the passage of a system through non-equilibrium states is called a **non-equilibrium process.** It is the result of *finite* action on a system that is in equilibrium. Violation of the interconnection between the system and its surroundings which imparted an impetus to the system and thus caused the appearance of a non-equilibrium process does not lead to its stopping. In other words, a non-equilibrium process, once started, will take place in an isolated system until a state of equilibrium sets in again. Thus, a non-equilibrium process is a *unidirectional* one. Owing to the finite rate of the process and the existence of losses (for instance for friction), the work done by the system is less than in an equilibrium process.

A system that has completed an equilibrium process can return to its initial position after passing in the reverse process through the same equilibrium states which it passed through in the forward process. This property of an equilibrium process is called its **reversibility.** Consequently, a thermodynamic process after which a system and the systems (surroundings) interacting with it can return to their initial state is called **reversible.**

If they cannot return to their initial state, i.e. if, as a result of the process in the forward and reverse directions, changes remain in the surroundings or in the system itself, the process is called **irreversible** *.

It is quite clear that irreversible processes include not only non-equilibrium, but also **pseudoequilibrium** ones, when a system does not perform the maximum work in passing through equilibrium states.

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* Do not confuse the concepts of thermodynamic reversibility and irreversibility with the corresponding concepts of chemistry.

The difference between irreversible (non-equilibrium) and reversible (equilibrium) processes * can be illustrated by the following examples.

1. Consider the expansion of a gas under a piston in a cylinder with perfect heat-conducting walls (the cylinder is in a thermostat). If the pressure of the gas is balanced by a finite number of identical weights having a finite mass, then when these weights are removed from the piston one-by-one, the volume of the gas will change each time by a definite amount. After the removal of each weight, the pressure will sharply drop and the gas will expand. As soon as the volume of the gas reaches a value corresponding to the new mass, equilibrium sets in in the system. Now the next weight is taken off. In the coordinates p versus V, this process will be depicted by a descending broken line (Fig. 1*a*) whose number of steps equals the number of weights removed from the piston.

Conversely, the addition of each weight results in a sharp growth in pressure and a reduction in volume; as soon as the volume of the gas becomes equal to that before the weights were removed, the process will stop. Consequently, returning of the system to its initial state (compression) by consecutively adding the same weights will be depicted by an ascending broken line. It is obvious that both the forward and the reverse processes are irreversible.

Let us conduct the same experiment with smaller weights (Fig. 1*b*).

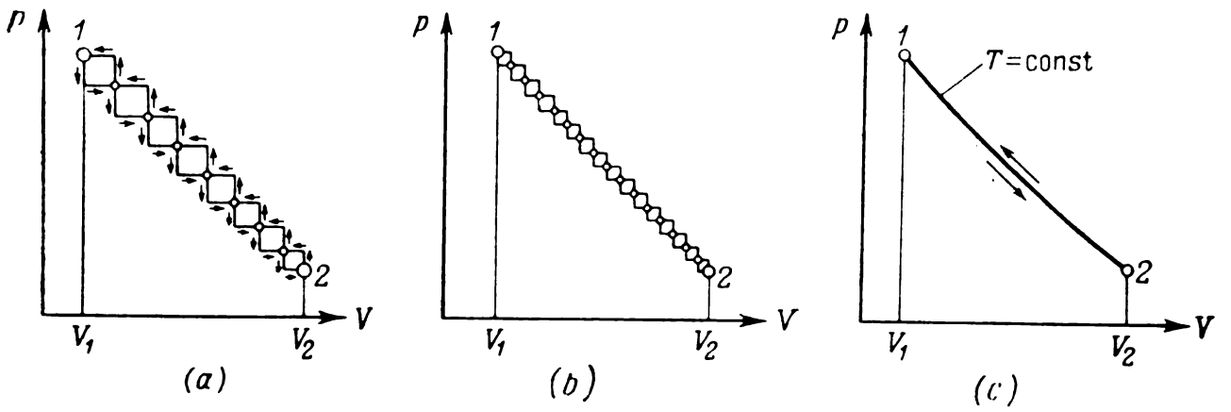

Fig. 1. Irreversible (*a*, *b*) and reversible (*c*) processes

Although in this case there are more points of contact of the two lines (characterizing the equilibrium state of the system), the process will again be irreversible.

In the limit, when the weights are infinitely small (and their number is infinitely great), the system continuously passes in

* We can speak of reversible or irreversible processes only for an isolated system. With respect to non-isolated systems, strictly speaking, the terms "equilibrium" and "non-equilibrium" should be used. But since the equilibrium of a process is a sufficient condition for its reversibility, we shall use chiefly the terms "reversibility" and "irreversibility" in the following.

both the forward and reverse directions through states of equilibrium. Such a process, shown in Fig. 1*c*, will be reversible.

The work of an irreversible process is

$$W_{\text{irrev}} = \sum_{V_1}^{V_2} p_i \Delta V_i$$

where p_i = external pressure

ΔV_i = change in volume corresponding to the given pressure (when the corresponding weight is removed).

When the degree of irreversibility diminishes, i.e. when the process approaches an equilibrium one, the number of terms of this sum grows, while the values of ΔV_i decrease. As a result, the work done by the system grows accordingly. In the limit, when the process becomes reversible and the number of terms $p_i \Delta V_i$ increases to infinity, each addend becoming an infinitely small quantity (since $\Delta V_i \to 0$), the work reaches its maximum value:

$$W_{\text{rev}} = \int_{V_1}^{V_2} p \, dV$$

It follows from Fig. 1 that the area numerically equal to the work of reversible expansion is the maximum (a comparison of a reversible process with an irreversible one has meaning only for the same initial and final states of a system, as was done in the given case).

If work is done on a system, then in a reversible process the work will be the minimum (the area under the curve in Fig. 1*c* is smaller than that under the ascending broken lines in Fig. 1*a* and *b*).

The work done in a reversible process (the minimum work) *equals the work received from a system in the same reversible process* (the maximum work). This can also be seen from Fig. 1*c*.

2. If the processes of charging and discharging accumulators were reversible, the curves of both processes would coincide. Actually, more work is spent for charging and less work is obtained in discharging than would be the case if these processes were reversible (Fig. 2).

Introducing the concept "reversible process" may seem unjustified. Only thermodynamically irreversible processes occur in nature, since all real changes take place in time (i.e. at a finite rate) with finite differences between the forces acting on a system and those opposing them, and are attended by various losses connected with friction, heat transfer, diffusion, radiation and the like.*

* Only near absolute zero, where irreversible effects become insignificant, do real processes approach reversible ones.

The following are examples of processes that are virtually the same as reversible ones:

(1) the motion of a piston separating two gases whose pressures differ from each other by a very small amount;

(2) crystallization from a saturated solution, where a negligible change in pressure or temperature leads to vaporization or conden-

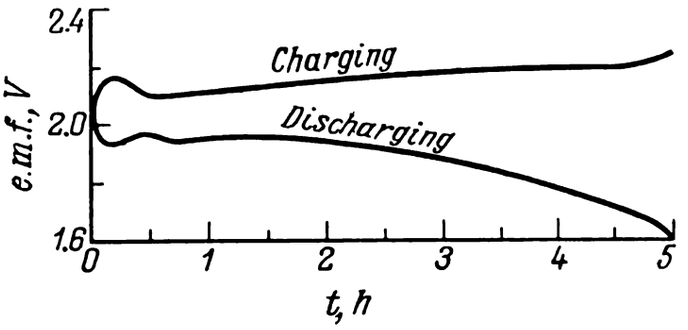

Fig. 2. Curves of charging and discharging of a lead-acid accumulator

sation of the solvent, and therefore to precipitation or solution of the substance;

(3) compensation of the e.m.f. of a galvanic cell by connecting to it another cell with its e.m.f. directed oppositely. In this case, a change in the e.m.f. by an amount of the order of magnitude of $\pm 10^{-6}$ V causes the reaction in the cell to proceed in the forward or the reverse direction.

However, thermodynamics, which is successfully applied to engineering problems, is a science dealing with *reversible* processes.

The expediency of using the concept of a reversible process is explained by a number of considerations.

First, any real process can always be represented as proceeding in conditions as close as desired to those of a reversible process (i.e. within the limits of experimental errors it can be considered reversible). This also explains why thermodynamics uses such concepts as an isolated system, an absolute vacuum, an ideal gas, an ideal solution, absolute zero of temperatures, and so on, i.e. various limiting notions.

Second, by comparing real and reversible processes, we can in each separate case establish the possibility of increasing the effectiveness of a process.

Third, only for a reversible process are thermodynamic parameters unambiguous and are thermodynamic calculations determining the changes in different properties of a system in a reversible process possible. These changes, owing to the independence of the change in the properties of a system on the path of the process, will coincide with the changes in the properties attending an irreversible process

(when the initial and final states of the systems coincide). Moreover, it is impossible to depict irreversible processes graphically; any point in the corresponding system of coordinates, for instance in the system p versus T, characterizing an equilibrium state, transforms into an indeterminate area for a system performing an irreversible process. This area, whose dimensions are the greater, the more the state of the system, differs from the equilibrium one, will include a group of points encompassing a certain interval of equilibrium states. This is why only a reversible process can be depicted graphically. Consequently, Fig. 1*a* and *b* are hypothetical illustrations of the indeterminacy of the values of p and V between the corresponding equilibrium states of the system.

The problem of the reversibility and irreversibility of processes is connected with the second law of thermodynamics, which will be considered later (see Chap. 4).

Example 1. A cylinder contains a weightless piston under which there is a gas and over which there is a vacuum. A row of bars are inserted into the walls of the cylinder along its height, and the lowermost bar holds the piston in place. When these bars are removed one-by-one from the bottom upward, the piston moves and the gas expands. Will this process be a reversible one if the bars are arranged at an infinitely small distance from one another and the piston moves without friction?

Solution. The above process will be a pseudoequilibrium one, and, therefore, irreversible, since the gas upon its expansion performs no work (there is no counterpressure). For the process to become reversible, the bars should be replaced with a weight and the piston gradually loaded, simultaneously supplying heat equivalent to the work done by the gas.

1.2.5. Mathematical Relations Between the Parameters of State

The independence of a change in a property of a system on the nature of the process in it means that *an infinitely small change in a property is a full differential.* We shall prove this postulate. Let z be a property of a system determined by two other properties x and y, i.e. $z = \varphi(x, y)$. Hence the expression

$$dz = M\,dx + N\,dy \tag{1.1}$$

in which M and N are also functions of x and y, is a full differential. This means that

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{1.2}$$

Comparison of Eqs. (1.1) and (1.2) shows that

$$M = \left(\frac{\partial z}{\partial x}\right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y}\right)_x \tag{1.3}$$

hence

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial y\, \partial x} \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x\, \partial y} \tag{1.4}$$

But the value of the derivatives does not depend on the order of differentiation, therefore

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{1.5}$$

This is the proof of the *first* theorem on the full differential.

If M and N from Eq. (1.1) do not satisfy Eq. (1.5), then dz is not a full differential — this is the reverse theorem which is also not difficult to prove. In this case, the binomial being considered is simply a certain infinitely small quantity; in other words z is not a property of the system.

The *second* theorem states that *if the integrand is a full differential, then the result of integration does not depend on the transition (integration) path, but is determined only by the coordinates of the final and initial points.*

Indeed, if $z = \varphi(x, y)$, then

$$z_2 - z_1 = \int_1^2 dz = \int_1^2 d\varphi(x, y) = \varphi(x_2, y_2) - \varphi(x_1, y_1) \tag{1.6}$$

The reverse theorem is also easily proved.

The *third* theorem follows as a corollary of the second : *the integral of a full differential when integrating over a closed contour equals zero.* Its reverse theorem also follows from the second one and states that *if an integral taken over a closed contour equals zero,* i.e. if

$$\oint dz = 0 \tag{1.7}$$

then the integrand is a full differential.

The preceding equations contained only two variables. We are limiting our discussion only to this case, because, as will be seen from the following, it is the most widespread one.

Since most thermodynamic processes take place in conditions when one of the parameters is constant, then partial derivatives

are widely used in thermodynamics. They are related by the equation *

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1 \tag{1.8}$$

This expression, which makes it possible to find any of the derivatives when the others are known, and which corresponds to the functional relationship $\varphi(x, y, z) = 0$, can be written down in different ways, since any of the partial derivatives can be taken as the first multiplier. If attention is given to the order of changing the letters corresponding to the three variables in Eq. (1.8), then it will not be difficult to write down the subsequent partial derivatives.

Example 2. The relationship $U = \varphi(V, T)$, where U is the internal energy of a system, is known. What will be the form of the equation relating a change in U to a change in p and T if the relationship $V = \varphi(p, T)$ is known?

Solution. On the basis of Eq. (1.2) we have

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

and

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT$$

Substituting for dV in the first equation its value from the second one, we get

$$dU = \left(\frac{\partial U}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT\right] + \left(\frac{\partial U}{\partial T}\right)_V dT$$

or

$$dU = \underbrace{\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T}_{\left(\frac{\partial U}{\partial p}\right)_T} dp + \underbrace{\left[\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial U}{\partial T}\right)_V\right]}_{\left(\frac{\partial U}{\partial T}\right)_p} dT$$

* When $z = \text{const}$, Eq. (1.2) acquires the form

$$0 = \left(\frac{\partial z}{\partial x}\right)_y (\partial x)_z + \left(\frac{\partial z}{\partial y}\right)_x (\partial y)_z \quad \text{or} \quad 0 = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x$$

Multiplying both parts of the latter equation by $(\partial y/\partial z)_x$, we get Eq. (1.8).

In a similar way we can also pass over from one series of independent variables to another in other cases.

Example 3. Show that the quantity $dz = x\,dy + y\,dx$ is a full differential.

Solution. It follows directly from Eq. (1.5) that dz is a full differential. This can also be confirmed graphically.

Imagine a number of curves plotted in the system of coordinates y versus x and joining certain points *1* and *2* (Fig. 3).

For any of these curves the integral

$$\int_1^2 (x\,dy + y\,dx) = \int_1^2 d(x, y)$$

will have the same value equal to the sum of two areas, one of which is formed by the given curve, two vertical lines dropped to the axis of abscissas from points *1* and *2*, and the axis of abscissas; the other one is formed by the given curve, two horizontal lines drawn from the same points to the axis of ordinates, and the axis of ordinates. Consequently, the total change in z when passing from *1* to *2* along any of the curves and returning to the initial point along a different path should be, according to Eq. (1.7), equal to zero.

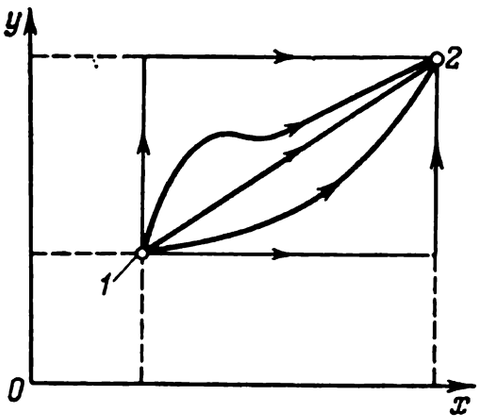

Fig. 3. Graph showing that a change in properties does not depend on the nature of a process. (See Example 3)

We shall make the calculations more concrete.

Suppose that one mole of a gas, for instance methane, is considered as the system, and the temperature, pressure and a property called the enthalpy H (see Sec. 2.2) are taken as the variables x, y and z, respectively. Assume that the system passes from point *1*, characterizing the state of the system having the properties T_1, p_1 and H_1, to point *2*, corresponding to the state of the system with the properties T_2, p_2 and H_2, in two ways:

(1) isobaric heating to T_2 with the following isothermal compression from p_1 to p_2;

(2) isothermal compression to p_2 with the following isobaric heating from T_1 to T_2.

In both cases, the change in the enthalpy of the methane will be the same; in accordance with Eq. (1.6) it is

$$H_2 - H_1 = \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T}\right)_p dT + \int_{p_1}^{p_2} \left(\frac{\partial H}{\partial p}\right)_T dp$$

To obtain a numerical result, we must have the dependence of $(\partial H/\partial T)_p$ on T and of $(\partial H/\partial p)_T$ on p. These derivatives (see pp. 59 and 104) are $(\partial H/\partial T)_p = C_p$ and $(\partial H/\partial p)_T = V - T(\partial V/\partial T)_p$ (C_p is the heat capacity at constant pressure). Therefore

$$H_2 - H_1 = \int_{T_1}^{T_2} C_p dT + \int_{p_1}^{p_2} \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp$$

Consequently, to calculate $H_2 - H_1$ the first way, we must have the temperature dependence of the isobaric heat capacity of methane at the low pressure p_1 (for example 1 atm) within the temperature interval from T_1 to T_2 and the dependence of the volume of methane and the slope of the isobars on the pressure (within the interval from p_1 to p_2) at the high temperature T_2. To calculate $H_2 - H_1$ the second way, we need the values of $V = \varphi(p)$ and $(\partial V/\partial T)_p = \varphi(p)$ at the low temperature and $C_p = \varphi(T)$ at the high pressure.

Both ways of calculation should give identical results; for this reason the method is selected for which experimental data are available. Since the values of $C_p = \varphi(T)$ are generally not available for compressed gases and are not always sufficiently reliable when they are available (they are quite difficult to measure and calculate), then good practice dictates the choice of the first way.

Example 4. Show with the aid of Eq. (1.8) that the modulus of elasticity of a body $m = -\left(\frac{\partial p}{\partial V/V}\right)_T$ equals $\frac{\gamma p}{\alpha}$, where $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ is the isobaric cubic expansion coefficient, and $\gamma = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V$ is the isochoric pressure coefficient.

Solution. In accordance with Eq. (1.8), we have

$$\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

Multiplying and dividing the right-hand side of this equation by V, we get

$$\left(\frac{\partial p}{\partial T}\right)_V = -V\left(\frac{\partial p}{\partial V}\right)_T \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = m\alpha$$

Since $(\partial p/\partial T)_V = \gamma p$, then $m = \gamma p/\alpha$.

1.3. TERMS AND SYMBOLS

Since the mechanism of transformation is not considered in thermodynamics, the equations used to write down processes relate only the initial (left-hand side of the equation) and final (right-hand side) states of a system. Every chemical formula will denote not only the nature of a substance, but also its quantity (one mole).

The concentration of a substance in a mixture (solution) in the vast majority of cases is expressed in **mole fractions**

$$x_i \equiv \frac{n_i}{n_1 + n_2 + n_3 + \ldots + n_k} \tag{1.9}$$

i.e. by the number of moles of a given substance n_i related to the total number of moles $n_1 + n_2 + \ldots + n_k$ (see also Sec. 8.1).

When necessary, the chemical formula of a substance is followed by an abbreviated characteristic of its physical state in parentheses ("g" stands for gas, "lq" for liquid and "c" for crystalline or solid). Unless otherwise indicated, it is assumed that the substance is under a pressure of 1 atm and its state of aggregation corresponds to standard conditions.

When it is necessary to characterize a process, its equation will be attended by the notation $\Delta Y = \ldots$, which designates the increment of property Y when the system passes over from the initial state to the final one, i.e. $\Delta Y = \Sigma Y_{\text{fin}} - \Sigma Y_{\text{init}}$ (calculated per mole). Thus, when we write down

$$H_2O(c) = H_2O(lq), \quad \Delta V = -2 \text{ cm}^3$$

we mean that the melting of one mole of ice proceeding at atmospheric pressure and 0 °C is attended by a reduction in the volume equal to 2 cm³.

When we write down that $Y = \text{const}$, we mean only the constancy of the given property (owing to the limitation imposed on the system) and do not indicate the value of the constant quantity. For this reason throughout the text, the designation "const" is used without any subscripts. A single designation (φ) is also used to indicate any functional relationship.

A list of the most important symbols used in the book is given in Appendix 1.

Extensive quantities are generally measured in the relevant units per mole. For example, the units of V and S are cm^3/mol and cal/mol·K. When extensive properties are considered without regard to the quantity of substance instead of being related to one mole, we introduce no new symbols but merely imply that the given quantity corresponds to the total amount of substance (in a number of cases this is specially indicated).

References to the publications listed at the end of the book are given in brackets, the letter denoting the section of the list, and the number denoting the serial number of the relevant publication in this section.

Chapter 2

THE FIRST LAW OF THERMODYNAMICS

2.1. CONTENT OF THE FIRST LAW

The first law of thermodynamics is a particular case of the **law of conservation and transformation of energy** as applied to processes accompanied by the liberation, absorption or transformation of heat.

The law of conservation of energy was formulated many times for different kinds of mechanical motion in a qualitative (R. Descartes, 1640) and a quantitative (G. Leibnitz, 1697) forms. M. Lomonosov's experiments (1745-1746) approached a generalized definition of the principle of conservation of matter and motion which was later acknowledged as a general law of nature of primary significance. The law of conservation of energy was proved for the conversion of heat into work and vice versa in the works of H. Hess (1836), J. Mayer (1842), J. Joule (1847) and H. Helmholtz (1847).

The law of conservation and transformation of energy, according to F. Engels, expresses the fact that "the indestructibility of motion cannot be merely quantitative, it must also be conceived qualitatively" *, i.e. indicates the unlimited ability of one kind of motion to transform into another one.

2.1.1. Cyclic Processes

If in a number of systems, cyclic thermodynamic processes occur, and the balance of heat Q and work W has been calculated for each of them, then in accordance with the experimental results, regardless of the nature of a process and of a system, we have

$$\frac{\Sigma Q_1}{\Sigma W_1} = \frac{\Sigma Q_2}{\Sigma W_2} = \frac{\Sigma Q_3}{\Sigma W_3} = \ldots = \text{const} \qquad (2.1)$$

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* F. Engels. Introduction to Dialectics of Nature. In : K. Marx and F. Engels. *Selected Works in Three Volumes*, Vol. 3, p. 55. Moscow, Progress Publishers (1970).

where ΣQ_i = algebraic sum of the heats of all the processes in the i-th system

ΣW_i = algebraic sum of all the work done by the i-th system against *all* the forces acting on it (pressure, electromotive force, etc.)

const = **mechanical equivalent of heat** whose numerical value depends on the units used to measure Q and W; when the same units are used, it equals unity.

Equation (2.1) establishes the equivalence of heat and work.

In thermodynamics, Q and W are conventionally expressed in calories. In this case, the constant in Eq. (2.1) will equal one. With the selected rule of signs for Q and W, it will be positive.

Let us write down Eq. (2.1) in the generalized form:

$$Q = W \quad \text{or} \quad Q - W = 0 \tag{2.2}$$

where $Q = \Sigma Q_i$ and $W = \Sigma W_i$.

It follows directly from Eq. (2.2) that a machine cannot be built which would make it possible to increase the amount of energy in an isolated system. This formulation of the first law is often given in a more concise form, namely, *a perpetual motion machine (perpetuum mobile) of the first kind is impossible* *.

2.1.2. Non-Cyclic Processes. Internal Energy

For a non-cyclic process, we have $Q \neq W$, because apart from the conversion of heat into work a change occurs in the system itself. **

Assume that the transition of a system from state *1* to state *2* can be accomplished in several ways (see Fig. 3). Let us choose three and denote the balances of heat and work by Q_1 and W_1, Q_2 and W_2, and Q_3 and W_3, respectively.

Let us conduct two cyclic processes: (1) a forward transition along the first path and a reverse transition along the second path; and (2) a forward transition along the first path and a reverse transition along the third path. Both these processes do not depend on each other and can be written down in accordance with Eq. (2.2) by means of the equations

$$Q_1 + Q_2 = W_1 + W_2 \quad \text{and} \quad Q_1 + Q_3 = W_1 + W_3$$

* Back in 1775 the French Academy of Sciences stopped considering any projects of a perpetual motion machine. They were rejected by inserting the inscription "Consider that the project was not submitted" on their title page.

** An exception are processes of isothermal expansion (compression) of an ideal gas and certain chemical reactions.

Subtracting the first equation from the second, we get after transformation

$$Q_2 - W_2 = Q_3 - W_3$$

Let us extend the same reasoning to any number of cycles in which the forward paths coincide while the reverse paths returning a system to its initial state are different. In this case we get

$$Q_2 - W_2 = Q_3 - W_3 = \ldots = \text{const}$$

i.e. for a non-cyclic process the quantity $Q - W$ does not depend on the transition path, but is determined only by the initial and final states of the system.

In other words, the quantity $Q - W$ for any process is determined by the change in a certain property of the system. This property is called the **internal energy** (or **energy**). It is a function of state of the system characterized by the fact that its growth in any process equals the sum of the heat imparted to the system and the work done on it.

The absolute value of the energy cannot be determined, because it is impossible to bring a system to a state deprived of energy. This does not cause any practical inconvenience, however, since any process results in a *change* in energy. If desired, the energy can be counted from any state of a system by conventionally ascribing to it a value of the energy equal to zero.

The energy of a system is generally a function of its state and consists of three parts : (1) the kinetic energy of motion of the system as a whole ; (2) the potential energy due to the position of the system in an external field (on the condition that the thermodynamic state of the system does not change when it is moved in this field) ; and (3) the internal energy U.

In chemical thermodynamics, stationary systems are generally considered in the absence of an external field ; in this case the total energy of the system will equal the internal energy. The latter is the sum of : (a) the kinetic energy of molecular motion (translational and rotational) ; (b) the intermolecular energy, i.e. the energy of mutual attraction and repulsion of the particles forming the system ; (c) the intramolecular, i.e. chemical energy ; (d) the energy of electronic excitation ; (e) intranuclear energy ; (f) radiant energy ; and (g) gravitational energy due to the attraction of particles of a substance to one another.

In this case, the heat imparted to a system produces a change or increment in the internal energy $\Delta U = U_2 - U_1$ and goes to overcome the resistances preventing a change in the state of the system, i.e. to perform work.

Consequently

$$Q - W = U_2 - U_1 \quad \text{or} \quad Q = \Delta U + W \tag{2.3}$$

(Here, as throughout the book, it is assumed that Q, W and ΔU are expressed in identical units.)

For cyclic processes, $\Delta U = 0$, and Eq. (2.3) transforms into Eq. (2.2).

After considering Fig. 3, the derivation of Eq. (2.3) becomes more obvious. It should be remembered, however, that the diagram corresponds to a reversible process, whereas Eq. (2.3), like Eq. (2.2), covers both reversible and irreversible processes.

Although Eq. (2.3) is true only on the assumption that a system does not become mobile because of the heat supplied to it, it may be extended to cases when this assumption is violated, since the differences in the kinetic energy between the initial and final states of a system even with a considerable change in the velocity are not usually appreciable. For example, the consumption of heat to acquire a velocity even of 40 m/s is only 0.19 kcal/kg. For processes in turbines, however, where the velocities of the working fluid are several hundred metres a second, the kinetic energy of the stream cannot be neglected.

The energy of a system, as has already been indicated, consists of the energies of its constituent parts. It should be borne in mind that when a system can interact with its surroundings, energy changes may occur in the system.

In contrast to energy, heat and work are not functions of state of a system, since they are *different forms of the transfer of energy.* For this reason, heat and work can be related only *to a process,* and *not to a state.*

The dependence of heat and work on the nature of a process is obvious, for example, from the existence of heat engines. If work were determined only by the initial and final states of a system, then for any cyclic process — and engines are periodically functioning machines — it would equal zero.

We can give the following simple example to confirm that ΔU does not depend while Q and W do depend on the way of conducting a process : both in the reversible and irreversible isothermal expansion of an ideal gas $\Delta U = 0$, but in the first case $W = Q = RT \ln (V_2/V_1)$ while in the second case (upon expansion into a vacuum) $W = Q = 0$.

Consequently, we cannot speak of heat as a form of energy (heat energy), a store of heat, an increment of the heat of a body, etc.

Such expressions, often encountered in scientific literature and not always avoided by the author, were inherited from the substance theory of heat, which explained thermal phenomena by the presence

of a special substance — thermogen. It was assumed that the amount of thermogen does not change, but is only redistributed between the bodies undergoing heat exchange.

The popularity of the thermogen theory was considerably increased by calorimetry, which evolved in the second half of the 18th century. Calorimetry seemed to permit heat to be measured. Precisely at that time, the terms "heat capacity" and "latent heat" (i.e. the heat of an isothermal process) were introduced. We now recommend "heat of vaporization" instead of "latent heat of vaporization", but the term "heat capacity", notwithstanding its inherent inconsistency, is still in use.

The honour of discovering the true nature of heat belongs to M. Lomonosov (1745), who forestalled the science of his time by a whole century. In "Discussion of the Solid and Liquid States of Bodies" (1760), he summarized the results of his previous experiments: "I have first of all proved (in the discussions on the causes of heat and cold) that Aristotle's elementary fire, or, according to the style used by present-day scientists, the special heat-generating matter, is only fiction; I have also confirmed that fire and heat consist in the continuous motion of particles forming the substance of a body." * Lomonosov's views or heat as a form of motion of particles together with his atomistic ideas led him to the kinetic theory and to the establishment of the nature of the gaseous state.

Lomonosov's great merit consists not only in that the ideas he developed were the first scientific theory of heat, but also in that he generally negated the existence of specific substances and thus conceived the unity of the "forces of nature" (whereas 17 years later A. Lavoisier included light and heat in his list of elements).

The interpretation of heat and work as forms of energy transfer is in complete agreement with Eq. (2.3). Rewriting it in the form

$$\Delta U = Q + (-W)$$

we conclude that the energy of a system changes as a result of the transfer of energy from the surroundings and that this is done only in two forms, heat and work. Thus, the analogy between heat and work following from the first law of thermodynamics is that heat and work are forms of the transfer of energy.

Here their similarity ends, however. Work is a **macrophysical,** i.e. ordered, form of the transfer of energy from the system doing work to the system over which it is being done; heat, on the contrary, is a **microphysical,** i.e. disordered, form of energy exchange between

* B. N. Menshutkin. *Trudy M. V. Lomonosova po fizike i khimii* (The Works of M. V. Lomonosov in Physics and Chemistry). Moscow-Leningrad, AN SSSR (1936). See p. 254.

systems owing to the chaotic (thermal) motion of particles. Work can be directed toward replenishing the stock of any kind of energy (electrical, magnetic, etc.); without being converted into work, heat can replenish the stock of only internal energy.

For this reason, the unit of energy adopted for heat and work does not prove that they are identical to energy in the same way as, for example, the identical dimension of entropy and heat capacity (see Appendix 1) does not indicate that they are identical.

The difference is rooted in the very nature of heat and work; although it is unimportant when analysing the first law, it has a fundamental significance when substantiating the second law of thermodynamics.

For an infinitely small change in the state, Eq. (2.3) becomes

$$\delta Q = dU + \delta W = dU + p\,dV + \delta W' \qquad (2.4)$$

where δW is the sum of all the elementary work, i.e. in general, the work $p\,dV$ of overcoming the external pressure and the work $\delta W'$ against electrical, magnetic and other forces (known as **useful** * work).

This form of writing emphasizes the fact that if *an infinitely small change in the energy is a full differential*, then δQ and δW are only vanishingly small *amounts* of Q and W. They are not derivatives of a function, since there is no functional relationship between heat or work and the thermodynamic parameters of state of a system. Therefore, if $U = \varphi(V, T)$, then, for example, the function $Q = \varphi(V, T)$ is generally invalid.

Although the function of Q on V and T does not exist, the quantity $(\delta Q/\partial T)_V$, for example, does have a definite meaning, since in this case the nature of the change is definite. The same can be said about the expression $W_p = \varphi(V)$: if the path is given, then the work is determined only by the initial and final states of a system (in this case by the quantities V_1 and V_2). But owing to the *limitation* ($V = \text{const}$ or $p = \text{const}$), the quantities δQ_V and accordingly δW_p will not be full differentials, but only acquire properties of the latter.

If a system is acted upon only by a constant external pressure, while other forces are absent or their influence may be neglected, then Eq. (2.4) becomes

$$\delta Q = dU + p\,dV \qquad (2.5)$$

In this equation, p can be considered as the pressure in the system only for a reversible process. For an irreversible process, we have

* The conditional nature of this adjective must be noted since processes are possible in which it loses its literal meaning.

$p_{ext} \neq p_{syst}$; therefore, in expansion $\delta W < p_{syst}\, dV$, and in compression $\delta W > p_{syst}\, dV$.

For a finite isobaric process, Eq. (2.5) becomes

$$Q_p = \Delta U_p + p(V_2 - V_1) \tag{2.6}$$

In the following, unless otherwise indicated, Eqs. (2.3) and (2.4) will be used exclusively in the form of Eq. (2.5) or (2.6), since the vast majority of chemical processes proceed at a constant external pressure in the absence of any other action on the system.

Equations (2.2) and (2.3) hold for any system and can be used to analyse any physical or chemical process and any state of aggregation of a substance.

Example. Using Eq. (2.5) and the equation $U = \varphi(V, T)$, show that δQ is not a full differential.

Solution. Combining Eq. (2.5) and the equation

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

we get

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV$$

If δQ were a full differential, then according to Eq. (1.5) we would have the equation

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \quad \text{or} \quad \left(\frac{\partial p}{\partial T}\right)_V = 0$$

which is in general absurd.

2.2. ENTHALPY

In an **adiabatic** process ($\delta Q = 0$), Eq. (2.5) becomes $-dU = p\, dV$ or $\int_1^2 p\, dV = U_1 - U_2$, i.e. work is done at the expense of a decrease in the energy of the system.

Not every change determined by the condition $Q = 0$, however, can be acknowledged as adiabatic. This condition is essential, but not sufficient. A process may be attended by heat exchange and be characterized by the equation $Q = 0$ only because the supply

and the rejection of heat at its different stages mutually compensate each other.

The equation $Q = \text{const}$, which is a mathematical corollary of the equation $\delta Q = 0$, does not determine the adiabatic nature of a process, since Q is not a function of state and δQ is not a full differential. A body cannot contain a "reserve stock of heat".

In an **isochoric** process ($dV = 0$), Eq. (2.5) becomes

$$\delta Q_V = dU_V \tag{2.7}$$

or for a finite change it becomes

$$Q_V = \Delta U_V \tag{2.8}$$

For an **isobaric** process ($dp = 0$), Eq. (2.5) can be written down in the form

$$\delta Q_p = d(U + pV) \tag{2.9}$$

i.e. δQ_p is a differential of the function of state of a system H:

$$H \equiv U + pV \tag{2.10}$$

which according to definition equals the sum of the internal energy U and the product of the volume and the pressure.

The function H is called the **enthalpy** (from the Greek word "thalpos" — "to become heated"; this term was introduced by H. Kamerlingh-Onnes, 1909) *. Since the product of p and V equals the potential energy, H could have been called the "energy of an extended system".

For a finite process we have

$$\Delta H = \Delta U + \Delta(pV) \tag{2.11}$$

Differentiating Eq. (2.10) and combining the resulting expression with Eq. (2.5), we find

$$\delta Q = dH - V\,dp \tag{2.12}$$

and for a finite change we have

$$Q = \Delta H - \int_1^2 V\,dp \tag{2.13}$$

* The synonymous term "heat content" should not be used since it contradicts a proper notion of the nature of heat (we cannot speak about the content of heat in a body !).

When p = const, Eq. (2.12) becomes

$$\delta Q_p = dH_p \tag{2.14}$$

or for a finite change of the system

$$Q_p = \Delta H_p \tag{2.15}$$

Since Q depends on the path of the process, while ΔU and ΔH do not depend on it, then the subscripts in the left-hand sides of Eqs. (2.6-2.9, 2.14 and 2.15) mean X = const, and in the right-hand sides mean $X_1 = X_2$.

It follows from Eq. (2.15) that the enthalpy is particularly important in isobaric processes. It is clear, however, that in any process

$$\Delta H = H_2 - H_1 = (U_2 + p_2V_2) - (U_1 + p_1V_1)$$

Like Eqs. (2.5) and (2.6), Eqs. (2.12) and (2.13) are a mathematical formulation of the first law. The latter equations are more convenient when V and T are the independent variables, and the former when p and T are the independent variables. (The temperature is implicit in all the above equations.)

In accordance with Eq. (2.10), heating results in a growth of H (see also p. 59 et seq.). The similar rate of growth of H with T for two similar substances M and N makes it possible, within the limits of a constant state of aggregation of these substances, to use the approximate linear relationship

$$(H_T - H_{T_1})_N \approx A(H_T - H_{T_1})_M + B \tag{2.16}$$

in which their enthalpies H_T counted from the enthalpy at the basic temperature T_1 (in particular, $T_1 = 298.15$ K, Fig. 4) are compared at equal temperatures. The slope of the straight lines [A in Eq. (2.16)] changes regularly with a change in the atomic number of the element. This permits us to assess the temperature dependence of the enthalpy for RaO without having any experimental data at our disposal.

It is possible to use the relationship

$$\left(\frac{H_T - H_{T_1}}{T}\right)_N \approx A\left(\frac{H_T - H_{T_1}}{T}\right)_M + B \tag{2.17}$$

similar to the preceding one, and also the relationship (Fig. 5)

$$(H_T - H_{T_1})_{II} \approx A(H_T - H_{T_1})_I + B \tag{2.18}$$

(T_1 frequently equals 0 or 298.15 K).

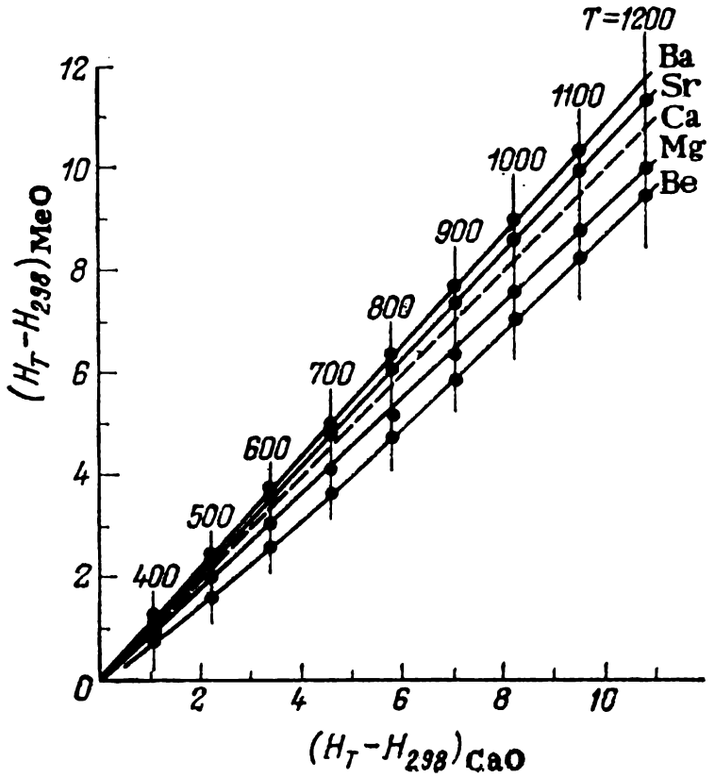


Fig. 4. Relationship between the enthalpies of CaO and oxides of other elements of subgroup IIA.

The points for BeO form a slightly curved line — here the influence of a certain falling out of the properties of compounds of the second-period element tells

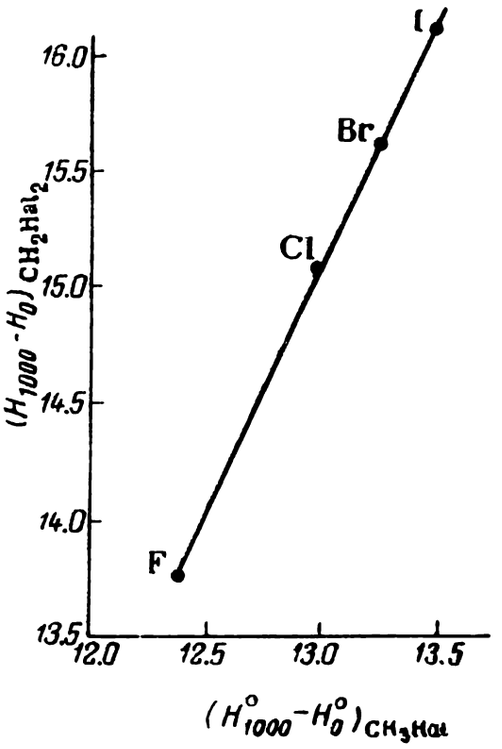


Fig. 5. Relationship between the enthalpies of $CH_3Hal(g)$ and $CH_2Hal_2(g)$:

Hal = F, Cl, Br or I

These relationships are specific examples of the fourth [Eqs. (2.16) and (2.17)] and the first [Eq. (2.18)] methods of comparative calculation, respectively [B45].

Chapter 3

HEAT EFFECTS AND HEAT CAPACITIES

3.1. HESS'S LAW

If a process is thermodynamically irreversible and proceeds at a constant volume or pressure, and *the products have the same temperature* as the reactants, then the heat liberated or absorbed during the process is called the **heat effect.**

The term "heat effect" of a process is not synonymous with the term **"heat of a process".** In accordance with Eq. (2.3), the heat of a process depends on the path which it follows, while the heat effect, in accordance with Eqs. (2.8) and (2.15), does not depend on it. In many cases, however (and sometimes also in this book) the term "heat of a process" is used for purposes of brevity.

The fact that the heat effect of a process does not depend on the path it follows was established experimentally by academician H. Hess in 1836. **Hess's law**, sometimes called the **law of constant heat summation**, is expressed mathematically by Eqs. (2.8) and (2.15) with the additional condition that $T_1 = T_2$ (owing to which the heat effects of chemical reactions could be called "latent" ones).

Hess's law states that *the heat effect of a process does not depend on the intermediate stages, but is determined only by the initial and final states of a system.* It is implied here that (1) the *only* work done by the system is work against the forces of the external pressure; (2) the pressure or volume during the *entire* process remains constant (for calorimetric measurements this corresponds to an open vessel or a closed bomb); (3) the process is thermodynamically irreversible. The second restriction is due to the fact that if the change in the intermediate pressures (volumes) does not affect the values of ΔH (or ΔU), then the value of Q changes.

Since isobaric processes are encountered most frequently in chemistry and chemical engineering, we shall use exclusively (unless otherwise specifically indicated) isobaric heat effects, i.e. ΔH in the following.

The relationship between the isobaric and isochoric heat effects is expressed by the equation

$$Q_p - Q_V = \Delta U_p + p\Delta V - \Delta U_V$$

which is obtained when combining Eqs. (2.8), (2.10) and (2.15). At low pressures we have $\Delta U_p \approx \Delta U_V$ (for ideal gases $\Delta U_p = \Delta U_V$), hence

$$Q_p - Q_V = p\Delta V \tag{3.1}$$

The relationship between Q_p and Q_V depends on the sign of $p\Delta V$. It may seem that Q_p is always greater than Q_V. This is true, however, only when a process is connected with an increase in the volume of a system, and for this reason additional heat is spent in doing external work (as a result, the value of Q_p becomes algebraically greater than that of Q_V).

It follows from Eq. (3.1) that the difference between Q_V and Q_p may be ignored, except for cases when gases participate in a reaction. The value of W is only a fraction of a per cent of ΔU for many processes, especially for all reactions between liquids and solids, and Hess's law can sometimes be applied without the restricting condition $p = \text{const}$ or $V = \text{const}$.

The following can be concluded from Hess's law.

1. The heat of formation of a compound from the reactants does not depend on the way in which this compound was obtained.

2. The heat of decomposition of a compound into the same reactants is equal in value and opposite in sign to the heat of formation of the compound from the same reactants.

3. If identical products are formed from two different systems as a result of different processes, then the difference between the values of the heat effects of these processes equals the heat of transition of the first system into the second one. If, on the other hand, a transition occurs from identical initial states to different final states, the difference between the values of the heat effects of the processes equals the heat of transformation of one set of products into another one. Hence two more corollaries follow, which are widely used.

4. *The heat effect of a reaction equals the algebraic sum of the heats of formation of the reactants from simple substances* *, i.e. the sum of the heats of formation of the products less the sum of the heats of formation of the reactants:

$$\Delta H = \Sigma(\Delta H_{\text{form}})_{\text{pr}} - \Sigma(\Delta H_{\text{form}})_{\text{r}}$$

5. *The heat effect of a reaction equals the algebraic sum of the heats of combustion of the reactants to identical products,* i.e. the sum of

* The term "enthalpy of formation", which is a conventional abbreviation of the expression "change in enthalpy during a reaction of formation" is often used instead of the term "heat of formation", i.e. the isobaric heat effect of a chemical reaction of formation of a given substance from the corresponding simple substances (by the latter are meant atoms or molecules of elements).

the heats of combustion of the reactants less the sum of the heats of combustion of the products:

$$\Delta H = \Sigma(\Delta H_{comb})_r - \Sigma(\Delta H_{comb})_{pr}$$

These two corollaries are illustrated in Fig. 6. In all cases the stoichiometric coefficients are taken into account, and it is understood that all the heat effects relate to identical states of aggregation of the elements.

Many important practical problems can be solved on the basis of the conclusions drawn from Hess's law. We shall indicate two of them.

1. Calculation of the heat effects of reactions inaccessible for direct measurement, for example the heat effect of the synthesis of hydrocarbons from simple substances or of the reaction

$$C + \frac{1}{2}O_2 = CO$$

$[\Delta H = (\Delta H_{comb})_C - (\Delta H_{comb})_{CO}]$.

2. Calculation of the heat effects of reactions difficult to carry out in a calorimeter. The slow rate of many processes precludes sufficiently reliable results since the heat will be partially dissipated (the transition of a substance from one modification to another one).

The calculation of the heats of reaction of organic compounds whose direct measurement is usually either difficult or completely impossible to perform is of special importance. In such cases, the calculations are usually conducted using the values of ΔH_{comb}. Owing to the incommensurability of the heat of a reaction and the heat of combustion of the reactants, the results of the calculations may be unsatisfactory. Errors in the measurement of ΔH_{comb} amounting even to tenths of a per cent may lead to enormous errors in the heat of a reaction. Isomerization processes are examples of such reactions. Thus, for the transition of *n*-heptane into 3-ethyl pentane, the value of ΔH is approximately 0.1% of that of ΔH_{comb}. If we assume that the error of the experimental data does not exceed 0.02-0.03% (the heat of combustion of only a few substances has

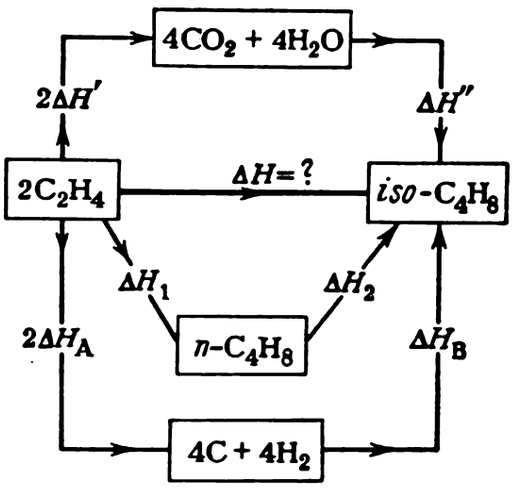


Fig. 6. Examples of applying Hess's law:

$\Delta H = \Delta H_1 + \Delta H_2 = 2\Delta H_A + \Delta H_B =$
$= (\Delta H_{form})_{iso\text{-}C_4H_8} - 2(\Delta H_{form})_{C_2H_4} =$
$= 2\Delta H' + \Delta H'' = 2(\Delta H_{comb})_{C_2H_4} -$
$- (\Delta H_{comb})_{iso\text{-}C_4H_8}$
(the attachment and detachment of oxygen have been omitted)

been measured with such a high accuracy at present), then the error in determining ΔH reaches 20-30%. In such cases, it is good practice to resort to the direct measurement of the heat effects, since their comparatively low values make it possible to obtain a considerably lower absolute error if the relative error made in determining them is the same as when finding ΔH_{comb}. For instance, scientists have succeeded in determining the heats of isomerization and hydrogenation of certain hydrocarbons with a high accuracy.

The use of Hess's law is based on the fact that we can work with thermochemical equations, i.e. with equations of reactions for which the numerical values of the heat effects are indicated, in the same way as with algebraic ones.

The calculations are often performed as follows. The algebraic operations which must be performed to get the necessary equation from the equations given are defined. Next similar algebraic operations are performed with the heat effects corresponding to the given reactions, and the necessary quantity is obtained. Such a method of calculation may cause difficulties when many auxiliary reactions are given for finding the heat effect. For this reason, one should never select the operations with the equations mechanically, but conduct the process mentally in terms of the reactions available for solving the given problem, i.e. transform the reactants with the aid of some of the auxiliary reactions into intermediates, which are then transformed in terms of the unused reactions into the products. The possibility of conducting the auxiliary reactions in this case naturally plays no part. It is also possible to use the Hess cycle for the calculations.*

Example 1. Calculate the heat effect of the reaction

$$NH_3 + \frac{5}{4} O_2 = NO + \frac{3}{2} H_2O(g)$$

according to the following data:

$$(1)\ H_2O(g) = H_2O(lq); \qquad \Delta H_1 = -10\,519$$

$$(2)\ \frac{1}{2} N_2 + \frac{3}{2} H_2 = NH_3; \qquad \Delta H_2 = -11\,040$$

$$(3)\ H_2 + \frac{1}{2} O_2 = H_2O(lq); \qquad \Delta H_3 = -68\,315$$

$$(4)\ NO = \frac{1}{2} N_2 + \frac{1}{2} O_2; \qquad \Delta H_4 = -21\,570$$

* See, for example, M. Kh. Karapetyants. *Vvedenie v teoriyu khimicheskikh protsessov* (Introduction to the Theory of Chemical Processes), 2nd ed. Moscow, Vysshaya shkola (1975).

Solution. Let us mentally represent the reaction of oxidation of ammonia as follows. The ammonia decomposes into nitrogen and hydrogen; then the nitrogen and part of the oxygen form nitric oxide, while the hydrogen combines with the remaining oxygen to form water, which then transforms into vapour. Since the sum of these reactions is equivalent to the basic one, then, by also equating their heat effects, we get

$$\Delta H = -\Delta H_2 - \Delta H_4 + \frac{3}{2}\Delta H_3 - \frac{3}{2}\Delta H_1 = -54\,084 \text{ cal/mol}$$

3.2. STANDARD HEAT EFFECTS

An essential condition for thermochemical calculations is that all the heat effects be related to identical conditions. Otherwise their values will be incompatible and algebraic summation will be impossible. This circumstance is due to the fact that the heat effects depend on the temperature and to an insignificant extent on the pressure. *

The conventional practice is to use the values of the heat effects for $p = 1$ atm and $t = 25\,°C$, it being assumed that gases have the properties inherent in them when $p \to 0$. These values of the heat effects are called **standard** ones ** and are designated by ΔH°_{298}.

The introduction of the additional condition is dictated by the need to take into account the difference in the properties of various gases at $p = 1$ and $t = 25\,°C$ since, strictly speaking, in these conditions they do not have the properties of ideal gases and deviate from the ideal state to a *different* extent.

The notion of the ideal state of gases corresponding to the standard heat effect is illustrated in Fig. 7. If $t = 25\,°C$, then point A corresponds to the actual state of a given gas at $p = 1$ and this temperature, while point O corresponds to the above hypothetical state.

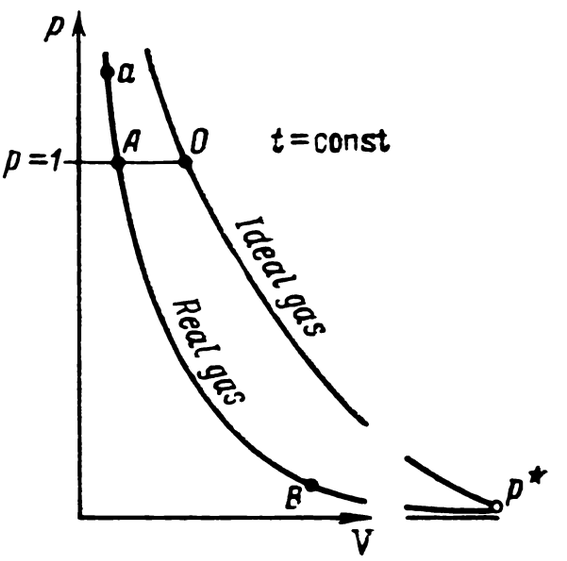


Fig. 7. Isotherms of a real and an ideal gases.
Illustrating the concept of the standard heat effect

* For reactions in solution, they also depend on the concentration (see Chap. 8).

** In the following, different standard quantities will be repeatedly used and will be designated by the superscript "°". The symbol $\Delta H^\circ_{T=298.15}$ will be replaced by ΔH°_{298} for purposes of brevity.

It can be achieved as a result of isothermal expansion to an infinitely low pressure p^* with the following isothermal compression along an isotherm of an ideal gas to $p = 1$. If points A and O are close to each other, it can be considered that the properties of a gas in standard conditions coincide with those of an ideal gas. When a gas deviates greatly from the ideal state, a correction must be made. The correction is very small, as a rule, but if a substance is in the form of a vapour, and the saturated vapour pressure at $t = 25\,°C$ considerably differs from $p=1$ (water vapour, point B, is an example), then the correction becomes appreciable and must be taken into account in precise calculations.

It should be noted that, except for a certain region of states, the enthalpy of a gas only slightly changes with a change in pressure, and in these cases the correction is negligible.

The choice of 25 °C (298.15 K) as the standard temperature is explained by the fact that many very important characteristics of processes have been determined at exactly this temperature. In addition, calorimetric measurements are also generally conducted at this temperature. Some of the older reference books give the heat effects for $p = 1$ atm and $t = 18\,°C$, but the difference of seven kelvins does not practically influence the heat effect.

The standard heats of formation refer to the states of elements that are **stable** in standard conditions (graphite, rhombic sulphur, white tin, liquid bromine, crystalline iodine, etc.). The standard heats of formation of ions in a solution are related to a gramme-ion concentration equal to unity, it being assumed that the solution has the properties of an infinitely dilute one. Here the heat of formation of a hydrogen ion is conditionally taken equal to zero. This convention vanishes when the heats of formation are summated. Thus, the sum $(\Delta H^\circ_{298})_{K^+}(aq) + (\Delta H^\circ_{298})_{NO_3^-}(aq)$ equals the actual heat of formation of these ions in an aqueous solution, i.e. the heat of formation of the compound in a solution when it *completely* dissociates.

The standard heat of combustion, unless otherwise indicated, corresponds to the combustion of C to CO_2 and of H_2 to $H_2O(lq)$. For other substances, the products of their oxidation are indicated in each case.

At present, the values of $(\Delta H^\circ_{298})_{form}$ are known for about 8000 objects (chemical compounds, free atoms, radicals, ions), including about 2000 organic substances. Much less data are available on $(\Delta H^\circ_{298})_{comb}$.

Tables 1 and 2 and Appendix 2 give the values of the standard heats of formation and combustion of selected substances. The most complete summary of various thermochemical quantities can be found in reference books (see Bibliography).

Table 1. **Standard Heats of Formation (in kcal/mol) of Selected Substances** *

Substance	ΔH°_{298}	Substance	ΔH°_{298}	Substance	ΔH°_{298}
		Inorganic Substances			
AgCl(c)	−30.73	FeS, α(c)	−24.0	NH_3(g)	−11.04
$AlCl_3$(c)	−168.3	FeS_2(c)	−39.0	NO(g)	21.570
C (diamond)	−0.437	HCl(g)	−22.06	NaCl(c)	−98.26
CO(g)	−26.416	HCl(aq)	−39.94	PbO_2(c)	−66.10
CO_2(g)	−94.052	HNO_3(lq)	−41.62	$PbSO_4$(c)	−220.04
$CaCO_3$ (calcite)	−288.45	H_2O(g)	−57.796	S (monocl.)	0.071
CaO(c)	−151.79	H_2O(lq)	−68.315	S_2(g)	30.477
Cl^-(aq)	−39.94	H_2S(g)	−5.0	SO_2(g)	−70.96
FeO(c)	−63.3	H_2SO_4(lq)	−194.6	SO_3(g)	−94.61
Fe_2O_3 (hematite)	−196.5	Mg^{2+}(aq)	−110.41	XeF_4 (monocl.)	−60
Fe_3O_4 (magnetite)	−267.0	$MgCl_2$(c)	−153.35		
		Organic Compounds			
CH_4(g)	−17.88	C_4H_{10}(g)	−29.810	C_6H_5COOH(c)	92.05
C_2H_2(g)	54.02	*iso*-C_4H_{10}(g)	−30.15	$CO(NH_2)_2$(c)	−79.53
C_2H_4(g)	12.54	C_6H_6(lq)	11.72	$C_6H_5NH_2$(lq)	7.43
C_2H_6(g)	−20.25	CH_3OH(lq)	−57.23	$C_{12}H_{22}O_{11}$(c)	−531.1
C_3H_6(g)	4.88	C_2H_5OH(lq)	−66.19		
C_3H_8(g)	−24.82	C_6H_5OH(c)	−39.44		

* See also Appendix 2.

It should be borne in mind that the compilation of precise tables requires the coordination of quantities related to one another by Hess's law. A more precise determination of individual heat effects without revising other ones may even lead to worse results.

Example 2. Derive a formula for the approximate calculation of the higher calorific value of fuel having the following composition (in per cent by weight) : C% of carbon, H% of hydrogen, S% of sulphur and O% of oxygen.

Solution. Assume that each of the combustible constituents is in its elementary form, owing to which the calorific value of the fuel will be the sum of the heat effects of combustion of each of these elements taken in the amounts in which they are contained in the fuel. Consider that the carbon of the fuel is in the form of graphite (this leads to an underestimated result). If we take into account that part of the hydrogen is combined with oxygen to

Table 2. **Standard Heats of Combustion (in kcal/mol) of Selected Organic Substances** *

Substance	$(\Delta H^\circ_{298})_{comb}$	Substance	$(\Delta H^\circ_{298})_{comb}$
Hydrocarbons		$CH_3Cl(g)$	−181.63
$CH_4(g)$	−212.80	$C_6H_5Cl(lq)$	−743.38
$C_2H_2(g)$	−310.44	*Alcohols*	
$C_2H_4(g)$	−337.27	$CH_3OH(lq)$	−173.45
$C_2H_6(g)$	−372.80	$C_2H_5OH(lq)$	−326.86
$C_3H_6(g)$	−491.98	$(CH_2OH)_2(lq)$	−284.32
$C_3H_8(g)$	−530.60	$C_3H_8O_3(lq)$, glycerine	−395.62
$C_4H_{10}(g)$	−687.55	$C_6H_5OH(c)$	−279.82
iso-$C_4H_{10}(g)$	−685.63	*Aldehydes, ketones, ethers, esters*	
$C_5H_{12}(g)$	−845.15	$CH_2O(g)$	−134.67
n-$C_nH_{2n+2}(g)$, n-$C_nH_{2n+2}(lq)$	n = 6-20: −57.909 − 157.44n; −57.430 − 156.25n	CH_3COH	−278.83
$C_6H_6(lq)$	−780.98	CH_3COCH_3	−427.8
cyclo-$C_6H_{12}(lq)$	−936.86	$CH_3COOCH_3(lq)$	−381.60
$C_6H_5CH_3(lq)$	−934.39	$CH_3COOC_2H_5(lq)$	−534.98
p-$C_6H_4(CH_3)_2(lq)$	−1088.15	$C_2H_5OC_2H_5(lq)$	−650.98
$C_{10}H_8(c)$, naphthalene	−1232.44	*Sulphur-Containing Compounds*	
$C_{14}H_{10}(c)$, phenanthrene	−1686.06	$COS(g)$	−154.76
Acids		$CS_2(lq)$	−304.64
$HCOOH(lq)$	−60.67	*Nitrogen-Containing Compounds*	
$CH_3COOH(lq)$	−209.03	C_2N_2	−261.94
$(COOH)_2(c)$	−60.12	$CO(NH_2)_2(c)$	−151.05
$C_6H_5COOH(c)$	−770.26	$C_6H_5NO_2(lq)$	−738.90
$C_{17}H_{35}COOH(c)$	−2696.0	$C_6H_5NH_2(lq)$	−810.84
Halogen Derivatives		*Miscellaneous*	
$CCl_4(lq)$	−62.3	$C_6H_{12}O_6(c)$, glucose	−669.80
$CHCl_3(lq)$	−102.31	$C_{10}H_{16}O(c)$, camphor	−1408.94
		$C_{12}H_{22}O_{11}(c)$, saccharose	−1348.99

* The products are $CO_2(g)$, $H_2O(lq)$, $N_2(g)$, $HCl(aq)$ and $SO_2(g)$.

form water and that the heat effect of condensation of water should be taken into consideration for calculating the higher calorific value, then the necessary quantity in accordance with the data of Table 1 will be expressed by the formula

$$-Q = 78.3C + 341.59\left(H - \frac{O}{8}\right) + 22.16S \text{ kcal/kg}$$

Example 3. Find the heat of formation of $MgCl_2(c)$ if its heat of solution in an infinitely great amount of water is −36.8 kcal/mol, and the heats of formation of the ions $Mg^{2+}(aq)$ and $Cl^-(aq)$ are, respectively, −110.41 and −39.94 kcal/g-ion.

Solution. In accordance with Hess's law we have

$$\Delta H = 36.8 + (-110.41) + 2(-39.94) \approx -153 \text{ kcal/mol}$$

3.3. SOME METHODS OF CALCULATING HEAT EFFECTS

The heat effects of a comparatively small number of reactions can be found directly from the heats of formation and combustion owing to the small amount of available calorimetric data. Therefore, various methods for calculating the standard heats of formation and combustion will be of interest.

3.3.1. Heats of Formation

The synthesis of a compound from simple substances can be identified with the process of their sequential transformation into monoatomic gases and the formation of the compound from them. The first stage is connected with the expenditure of energy to break the bonds, and the second with the liberation of the energy of formation of the new bonds. For this reason, the heat of formation of a gaseous substance, in accordance with Hess's law *, is

$$\Delta H_{\text{form}} = [\Sigma(n_i E_i)_r + \Sigma s_i(\Delta H_{\text{subl}})_i] - \Sigma(m_i E_i)_{pr} \qquad (3.2)$$

where n_i and m_i = number of bonds of a given kind in the reactants and the compound

E_i = energy of the i-th bond

s_i = number of different atoms of crystalline elements

$(\Delta H_{\text{subl}})_i$ = corresponding heats of sublimation (atomization).

The values of the energies of breaking selected bonds are given in Table 3. These values were found from the heats of formation and combustion of compounds, and also from spectroscopic data. Their error is about 1-2 kcal. The heat effect of the first two or three members of a homologous series deviates considerably from the additive one. The lack of equivalence of identical bonds and their mutual influence apparently manifest themselves to a greater extent in the lower homologues than in the higher members of the series.

* It is quite obvious that the additivity on which this method is based is not related to Hess's law.

Table 3. **Energy E of Breaking Selected Chemical Bonds (in kcal/mol)**

Bond	Molecule	E	Bond	Molecule	E
As—As	As_4	15.1	C—N	Amines, nitroalkanes	65.9
As—Br	$AsBr_3$	51.8	C≡N	HCN, $(CN)_2$	207.9
As—Cl	$AsCl_3$	60.3	C—O	Alcohols, ethers	79.6
As—H	AsH_3	47.5	C=O	RCHO, RCOR'	168.7
As—I	AsI_3	33.1		CO_2	191.0
C—Br	Alkyl bromides	63.3	C≡O	CO	255.8
C—C	Alkanes	79.3	N—H	NH_3, amines	92.0
	RCHO, RCOR'	83.8	N—N	N_2O_4	42.5
	Benzene ring	116.4	N=O	Nitroalkanes	103.9
C=C	Alkenes	140.5	N≡O	NO	149.4
C≡C	Alkynes	196.7	O—Cl	Cl_2O	48.9
C—Cl	Alkyl chlorides	76.0	O—F	F_2O	45.0
	CCl_4, $CHCl_3$	75.8	O—H	H_2O	109.4
	$COCl_2$	74.4		Alcohols	104.7
C—H	Alkanes	98.7	O—O	H_2O_2	33.3
	Alkenes	99.4	S—Cl	S_2Cl_2	71.0
	Alkynes, $CHCl_3$, HCN	96.3	S—H	H_2S	86.8
	Benzene	100.7	S=O	SO_2	125.9
C—I	Alkyl iodides	47.2	S—S	S_2Cl_2	69.0

For cyclic structures, especially for complicated molecules, such calculations lead to unsatisfactory results. The above method is approximate, since apart from the uncertainty of the value of the heat of sublimation of carbon (about 171 kcal/g-atom) and the inaccuracy of the data on which the calculations of E_t are based, there is the basic fact that additivity is violated even in the case of the simplest compounds. *

The heats of formation of crystalline **inorganic compounds** can be calculated by recalling the fact that the heats of formation of a compound of an element with other elements of one series or one subgroup of D. Mendeleev's periodic table, related to one gramme-

* V. Tatevsky (1953) worked out a more accurate method of calculations by taking into account the difference in the bond energies depending on the nature of the grouping of the atoms directly surrounding the given bond. Thus, in hydrocarbons of the methane series, ten subtypes of bonds have to be distinguished for the bonds C—C, and four subtypes for the bonds C—H (for greater detail see [B103, 104]).

equivalent, are in the first approximation a linear function of the logarithm of the atomic number of these elements. This law, established by A. Kapustinsky (1948), corresponds to the expression

$$\frac{\Delta H^{\circ}_{\text{form}}}{w} \approx a \log Z + b \qquad (3.3)$$

where w = valence
Z = atomic number
a and b = empirical constants.

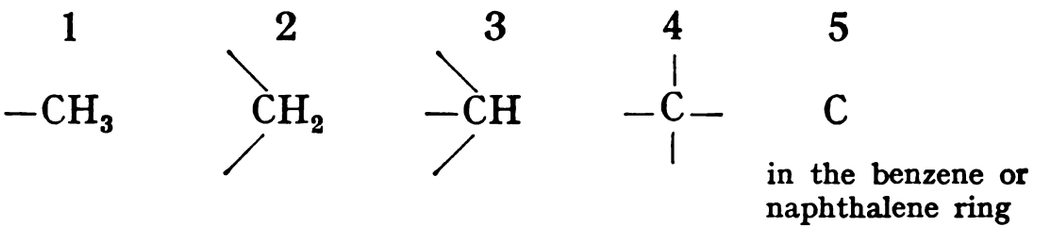
If we exclude compounds of elements that are at the beginning of the periods of the periodic table of elements (for example Na_2O in the series of oxides of the first group), coincidence with experimental data is often sufficiently satisfactory for rough estimation of the heats of formation of compounds which have not yet been studied.

The heats of formation of **organic compounds** *in the ideal gaseous state* can be found by summing the corrections ascribed to different groups in a molecule of the relevant compound [C4]. Every substance is assumed to consist of a main group which is modified by substituting other groups for the atoms forming it. The second column of the tables in Appendix 3 gives the following quantities needed for calculations:

(A) the heats of formation of the basic substances;

(B) corrections for substituting the group CH_3 for a primary hydrogen atom;

(C) corrections for substituting the group CH_3 for a secondary hydrogen atom (when the number of substitutions at one carbon atom is greater than one). [These corrections are based on the "type number" of the carbon atom at which substitution (A) has been made, and the "type number" of the adjacent carbon atom (C), the type number being determined according to the number of bound carbon atoms:



When there are several adjacent carbon atoms, the correction is chosen for the atom whose "type number" is maximum];

(D) corrections for substituting double or triple bonds for single ones;

(E) additional corrections;

(F) corrections for groups substituting the group CH_3.

The value of $\Delta H^{\circ}_{\text{form}}$ is generally calculated as follows. The substance is chosen that is the basis of the compound being considered. The value of $\Delta H^{\circ}_{\text{form}}$ is found for it, and corrections are added that

are the result of all the substitutions of hydrogen atoms by CH_3 groups needed to construct the carbon skeleton. (It is recommended first to construct the longest straight chain, and then the longest side chain. If the same compound can be obtained by different substitutions, the average result is taken.) After this, corrections are added for additional substitutions of hydrogen in other groups by CH_3 groups. Next, corrections are introduced for the bonds and for the substitution of the CH_3 groups by other ones.

Checking of this empirical method has shown that the results of the calculations differ from the most accurate experimental data by not more than 4 kcal/mol.

Example 4. On the basis of the data given in Appendix 3, calculate the standard heat of formation: (1) of *o*-dimethyl phthalate $C_6H_4(COOCH_3)_2$ and (2) of 2,2,3,3-tetramethylbutane (in the gaseous state).

Solution.

1. Basic substance (benzene)	19.82	Table A
Substitution of primary H by CH_3 group	−7.87	Table B
Substitution of H by CH_3 group in orthoposition	−7.41	Table B
Substitution of CH_3 group by COOH group	−87.0	Table F
Ditto	−87.0	Table F
Substitution of H in COOH by CH_3 group	9.50	Table C
Ditto	9.50	Table C
	−150.46 kcal/mol	

Calculation according to the heat of combustion gives the approximate value of −150 kcal/mol.

2. Basic substance (methane)		−17.89	Table A
Substitution of primary H by CH_3 group		−2.50	Table B
Substitution of secondary H by CH_3 group (Table C)	(A)	(B)	
CH_3 group in a four-member carbon chain	1	1	−4.75
	1	2	−4.92
Side CH_3 groups (clockwise—when the side groups are considered counterclockwise, somewhat different values are obtained)	2	2	−6.33
	2	3	−5.25
	3	3	−5.19
	3	4	−4.94
			−51.77 kcal/mol

This value differs from the most authentic value of −53.99 [B98] by 2.22 kcal/mol.

3.3.2. Heats of Combustion

D. Konovalov (1924) proposed the following approximate equation for gaseous substances:

$$(\Delta H^\circ_{298})_{comb} = -(48.80m + 10.60n + x) \text{ kcal/mol} \quad (3.4)$$

where m = stoichiometric number of oxygen atoms needed for the complete combustion of a given substance
n = number of moles of water formed
x = correction that is constant within the limits of a given homologous series and equals zero for saturated compounds.

By considering any organic compound as a hydrocarbon in which a certain number of hydrogen atoms are substituted by various atoms and groups of atoms, and by taking $(\Delta H^\circ_{298})_{comb}$ to be a function of the number of electrons passing over upon combustion to oxygen atoms, we get the approximate Kharasch formula (1929) for *liquid* organic substances:

$$(\Delta H^\circ_{298})_{comb} = -26.050(4C + H - n_e) + \Sigma k_i \Delta_i \text{ kcal/mol} \quad (3.5)$$

where 26.050 = heat of breaking of the C—C and C—H bonds and of the following formation of CO_2 and H_2O, kcal/mol·electron
$4C + H$ = number of migrating electrons for n-alkanes
n_e = number of partly displaced electrons in a molecule of a substance (for example in C_2H_6 we have $n_e = 0$, and in C_2H_5OH we have $n_e = 2$)
k_i = number of identical substituents
Δ_i = heat correction corresponding to the given substituent, which takes into account the change in the electronic structure of the n-alkanes because of polarization due to the introduction of a substituent.

Appendix 4 gives the values of Δ_i for different substituents and bonds. The sign of Δ_i is determined by the direction of motion of the electrons when the substituent is introduced. It is positive when electrons travel away from a carbon atom (in accordance with the diminishing of the energy of the molecule) and is negative when the electrons travel in the opposite direction.

Equation (3.5) holds on the assumption that the action of the substituent which is newly introduced into a molecule does not depend on the presence of other substituents. Consequently, it is assumed that each substituent increases or diminishes the value of $(\Delta H^\circ_{298})_{comb}$ by a certain constant quantity, i.e. the displacement of the electrons in a molecule induced by a substituent is disregarded.

3.3.3. Comparative Calculation of Heat Effects

Approximate calculations of ΔH for various reactions (including calculations of ΔH_{form} and ΔH_{comb}) can be conducted by using methods of comparative calculation [B45], particularly the first one, i.e. the relationship

$$\Delta H_{II} \approx A_1 \Delta H_I + B_1 \qquad (3.6)$$

in which the heats of the corresponding processes in two series (I and II) of similar substances (reactions) are compared in given conditions. Thus, the approximate equation

$$(\Delta H^\circ_{298})_{KHal} \approx 1.692(\Delta H^\circ_{298})_{AgHal} - 53.15$$

describes the relationship between the standard heats of formation of silver and potassium halides with a mean error of 0.4 kcal/mol. Figure 8 shows the application of expression (3.6) using two series of similar chemical processes as an example.

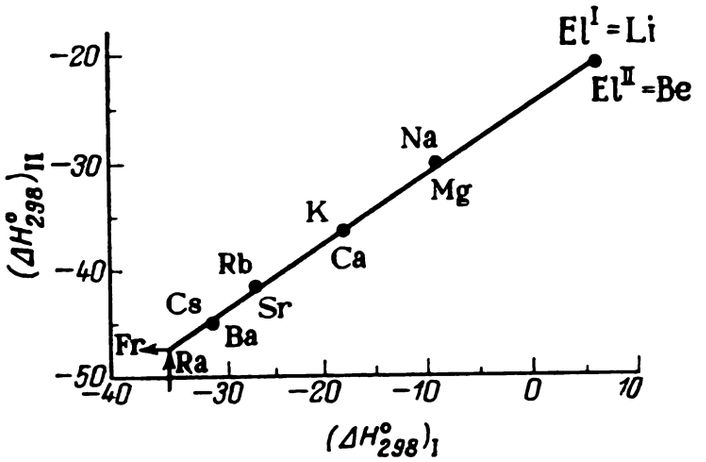


Fig. 8. Relationship between the standard heats of the reactions

I – $El^{II}(OH)_2 + CO_2 = El^{II}CO_3 + H_2O$;

II – $2El^{I}OH + CO_2 = El^{I}_2CO_3 + H_2O$

3.4. HEAT CAPACITY

3.4.1. Heat Capacity in Different Processes

The **mean heat capacity** of a homogeneous system is determined by the relationship

$$C_{T_1 \text{ to } T_2} \equiv \frac{Q}{T_2 - T_1} \qquad (3.7)$$

where Q is the amount of heat as a result of receiving (giving up) of which the temperature of the system grows (diminishes) from T_1 to T_2.

It is assumed here that the heating (cooling) causes neither a phase transition nor a change in the composition of the system.

The heat capacity corresponding to an infinitely small change in temperature, i.e.

$$C \equiv \frac{\delta Q}{dT} \tag{3.8}$$

is called the **true heat capacity.** The quantity $\delta Q/dT$ is not a derivative, because δQ is an infinitely small *amount* of heat.

The mean and true heat capacities are related by the equation

$$C_{T_1 \text{ to } T_2} = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} C \, dT \tag{3.9}$$

Because the amount of heat supplied depends on the nature of a process, the conditions of conducting it must be indicated to determine the heat capacity of gases. The heating (cooling) conditions do not have to be indicated for crystalline bodies and in most cases for liquids. One variable, the temperature, is generally sufficient to determine their heat capacity.

The value of the heat capacity varies within the limits from $+\infty$ (an isothermal process with the supply of heat) to $-\infty$ (an isothermal process with the removal of heat). For an adiabatic change we have $C = 0$.

Applying Eq. (3.8) to the most important processes, we get: for an isochoric process in accordance with Eq. (2.7)

$$C_V = \frac{\delta Q_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V \tag{3.10}$$

and for an isobaric process in accordance with Eq. (2.14)

$$C_p = \frac{\delta Q_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_p \tag{3.11}$$

It follows from Eq. (3.11) that

$$Q_p = \Delta H_p = H_{T_2} - H_{T_1} = \int_{T_1}^{T_2} C_p \, dT \tag{3.12}$$

This equation shows the expenditure of heat for the isobaric heating of a substance from T_1 to T_2. It should be noted that although

this quantity is designated in the same way as the heat effect, it naturally does not coincide with the latter.

Extending this temperature interval to from 0 K to T and taking into account the possibility of phase transitions, we get the following equation instead of Eq. (3.12):

$$Q_p = \Delta H_p = H_T - H_0 = \int_0^{T_{tr}} C^c_{p_I}\, dT + \Delta H_{tr} + \int_{T_{tr}}^{T_m} C^c_{p_{II}}\, dT + \\ + \Delta H_m + \int_{T_m}^{T_b} C^{lq}_p\, dT + \Delta H_{vap} + \int_{T_b}^{T} C^g_p\, dT \qquad (3.13)$$

This form of writing down the equation assumes that in the course of heating, a substance consecutively passes from one crystalline modification to another, then melts, boils, and the saturated vapour is superheated. In Eq. (3.13), the odd terms express the increase in

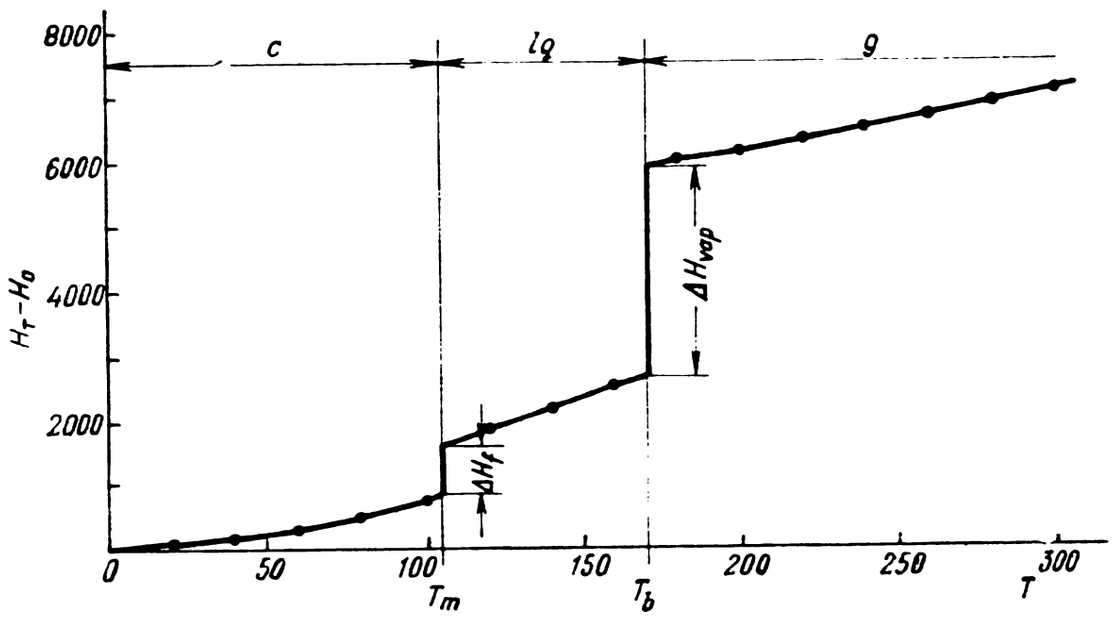


Fig. 9. Temperature dependence of enthalpy of ethene

enthalpy due to heating the given phase, and the even terms express this increase due to aggregate transitions. Relationship (3.13) is shown in Fig. 9 for a concrete example (this graph was constructed on the basis of Fig. 10). Equation (3.12) is obviously a particular case of Eq. (3.13).

Equation (3.13) is the basis for constructing various heat diagrams and tables for pure substances, mixtures and solutions.

The mean isochoric and isobaric heat capacities can be expressed by means of Eq. (3.7) with substituting of $Q_V = \Delta U_V$ or $Q_p = \Delta H_p$ for Q.

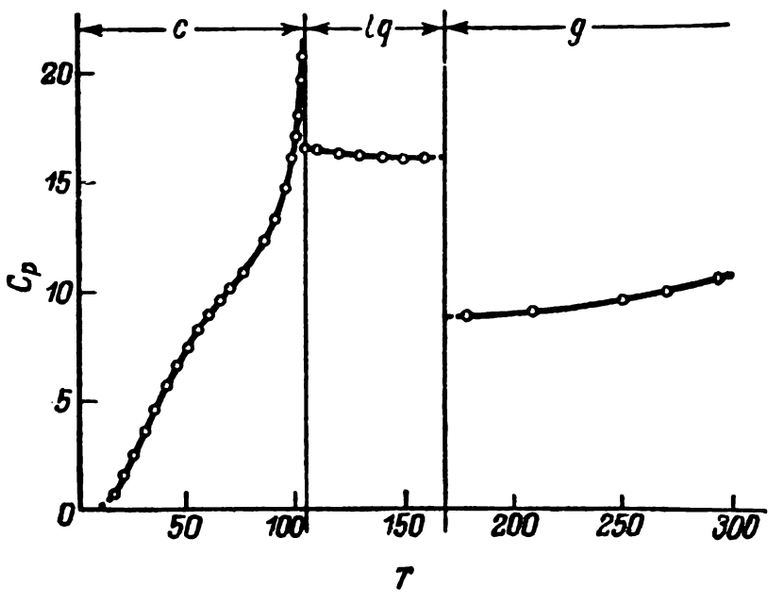


Fig. 10. Temperature dependence of heat capacity of ethene

We find the relationship between C_p and C_V from Eqs. (3.10), (3.11) and (2.10):

$$C_p - C_V = \left[\frac{\partial(U+pV)}{\partial T}\right]_p - \left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V$$

Assuming V and T to be the independent variables, we get

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

whence

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

Hence we finally have

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p \qquad (3.14)$$

Equation (3.14) has limited use, since the quantity $(\partial U/\partial V)_T$ is usually unknown.

The above equations may be applied for any system if the only force acting on it is the external pressure, and if an increase in the temperature does not result in the action of other forces.

3.4.2. Temperature Dependence of Heat Capacity

Crystals. We shall consider several equations for determining the temperature dependence of heat capacity.

Einstein Equation. According to the quantum theory, the energy of a linear oscillator is expressed by the equation

$$\varepsilon = \frac{h\nu}{e^{h\nu/kT} - 1} = k \frac{\beta\nu}{e^{\beta\nu/T} - 1}$$

where h = Planck constant
ν = frequency of vibrations characteristic of each substance
k = Boltzmann constant
$\beta = h/k$.

By extending the quantum theory to the vibrations of atoms of solid crystalline bodies and by taking into account that unlike a linear oscillator the number of degrees of freedom in a crystal equals three, we find for one gramme-atom of an element

$$U = 3R \frac{\beta\nu}{e^{\beta\nu/T} - 1}$$

Differentiation of this equation with respect to T gives the **Einstein equation** (1907)

$$C_V = 3R \frac{(\beta\nu/T)^2 e^{\beta\nu/T}}{(e^{\beta\nu/T} - 1)^2} \tag{3.15}$$

from which it follows that the value of C_V grows with increasing temperature.

The frequencies of vibrations needed to calculate the heat capacities can be found in several ways (according to the spectra, the compressibility, etc.). The simplest way is to compute the frequency by the equation

$$\nu = 2.8 \times 10^{12} \sqrt{\frac{T_m}{MV^{2/3}}}$$

which is obtained on the assumption that the amplitude of vibrations of the particles forming a crystal rapidly grows with increasing temperature until it becomes equal to the distance between separate particles. When this occurs, destruction of the crystal, i.e. melting of the substance, begins.

Expanding $e^{\beta\nu/T}$ into a series * and disregarding all the terms of the series except the first two because of the small magnitude of the exponent, we get

$$\lim_{\beta\nu/T \to 0} C_V = 3R$$

* $e^{+x} = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$.

With lowering of the temperature, C_V diminishes, and

$$\lim_{\beta\nu/T\to\infty} C_V = 0$$

Experimental data show that Eq. (3.15) gives good results for comparatively high temperatures. For medium and particularly low temperatures, the calculated values are less than the experimental ones, i.e. as absolute zero is approached, C_V does not diminish as rapidly with decreasing temperature as is required by Eq. (3.15). These discrepancies are due to the assumptions made in deriving Eq. (3.15) that the atoms of crystalline bodies vibrate independently of one another. This assumption, especially for low temperatures, cannot be justified owing to the close arrangement of the vibrating particles. For this reason, C_V should be calculated according to a polynomial equation, each member of which corresponds to a group of atoms having the same frequency of vibrations. The semi-empirical equation

$$C_V = \frac{3}{2} R \left[\frac{(\beta\nu/T)^2 e^{\beta\nu/T}}{(e^{\beta\nu/T} - 1)^2} + \frac{(\beta\nu/2T)^2 e^{\beta\nu/2T}}{(e^{\beta\nu/2T} - 1)^2} \right]$$

is sufficiently accurate, since calculations by Eq. (3.15) (where $\nu/2$ is substituted for ν) give a result which is approximately the same number of times greater than the experimental data by which the result obtained according to Eq. (3.15) is less than these data.

Let us denote the quantity $\beta\nu$ by Θ; it has the dimension of temperature * and is called the **characteristic temperature**, since it includes the frequency of vibrations characteristic of a given substance. The softer a substance, the smaller is the value of Θ. Its value is quite large for hard substances; for example for lead $\Theta = 87.2$, and for carbon (diamond) $\Theta = 1860$ K.

It follows from Eq. (3.15) that heat capacity is an unambiguous function of T/Θ, i.e. at equal values of this dimensionless quantity heat capacities of different substances should coincide. Consequently, if the temperature dependence of the heat capacity for every substance is depicted by its own curve (Fig. 11), then when the temperature is expressed in fractions of Θ we get a single curve for all the substances obeying Eq. (3.15) (Fig. 12). We can reach this conclusion purely empirically: when examining the graph of C_V against T (Fig. 11) the noticeable similarity of the curves points to the possibility of making them coincide when the scale along the x-axis is properly chosen, i.e. if we change from ordinary to "reduced" temperatures. The plot of C_V against T/Θ considerably simplifies

* $\beta\nu = \frac{h\nu}{k} = \frac{|\text{erg}\cdot\text{s}||\text{s}^{-1}|}{|\text{erg}\cdot\text{K}^{-1}|} = \text{K}.$

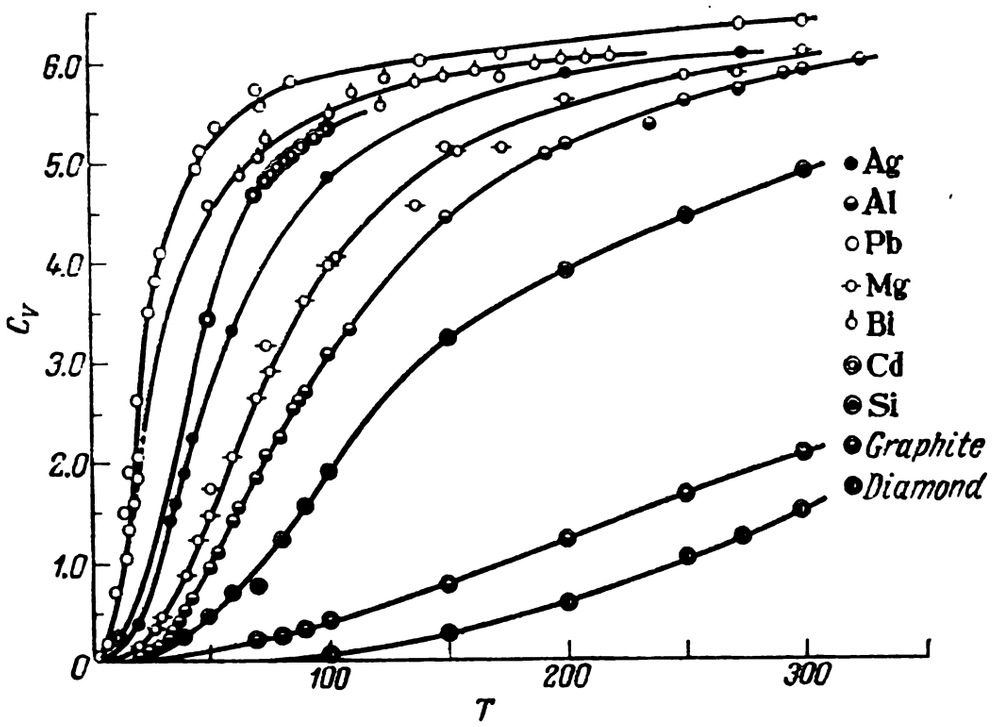


Fig. 11. Temperature dependence of heat capacity of selected crystalline substances at low temperatures

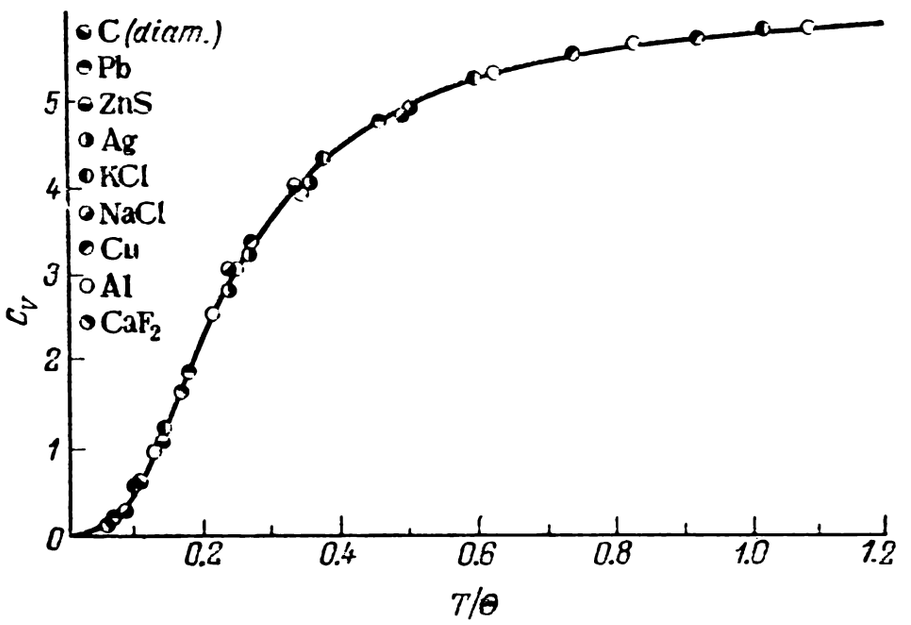


Fig. 12. Dependences of heat capacity of selected crystalline substances on T/Θ

calculations. Having a single value of C_V, it is simple to determine T/Θ and then Θ. After this, reverse calculations permit us to find the value of C_V for any temperature. It is more convenient to use tables of the **Einstein functions** for calculations (see Appendix 5) since they give the value of C_V per oscillator. The tabulated values should be tripled.

The simplest way to determine the quantity C_p is by the empirical equation

$$C_p = C_V + \frac{0.0214C_p^2T}{T_m} \approx C_V \frac{1 + 0.0214C_VT}{T_m} \tag{3.16}$$

At low temperatures, the difference $C_p - C_V$ is small, and when T is below 50 K it may be disregarded.

Debye Equation. Proceeding from the idea of the relationship between the thermal motion of the atoms in a crystal and its natural acoustic vibrations, a crystal lattice is considered as a system in which separate atoms (ions) are bound by quasi-elastic forces.

Near absolute zero, the amplitude of vibrations of atoms is very small, since the energy of the bonds retaining the elements of the crystal lattice is infinitely greater than the energy of the thermal motion causing the atoms to vibrate in the crystal. For this reason, it behaves like an absolutely elastic body, i.e. the substance can be considered as a continuous medium (a continuum), without regarding its atomistic nature. The close interaction of the particles results in a spectrum of frequencies from the minimum value of $\nu = 0$ to the maximum value ν characteristic of each substance. After calculating the energy and the heat capacity of such a system (replacing integration with expansion into a series and retaining only the first member of the series), and then performing the essential transformations and simplifications, we get the **Debye equation** (1912)

$$C_V = \frac{12R\pi^4}{5}\left(\frac{T}{\beta\nu}\right)^3 = 464.5\left(\frac{T}{\Theta}\right)^3 = aT^3 \tag{3.17}$$

It is more accurate than Eq. (3.15) and is the most reliable upon extrapolation to the region of low temperatures down to absolute zero [the mean error of calculations at $\Theta/T > 12$ for substances for which Eq. (3.17) holds is about 1%].

The calculations can be performed with the aid of tables of the **Debye functions**, which, like the tables of the Einstein functions, give the dependence of C_V on Θ/T (see Appendix 6).

Tarasov Equations. V. Tarasov showed (1950) that the following equations hold for laminar structures (flat crystals) and chain structures (unidimensional crystals), respectively, at low temperatures:

$$C_V = 43.272\left(\frac{T}{\Theta_2}\right)^2 = bT^2 \tag{3.18}$$

and

$$C_V = \pi^2 R\frac{T}{\Theta_1} = cT \tag{3.19}$$

Laminar structures include mica; unidimensional crystals include linearly polymerized molecules, for example rubber *, quartz and polyatomic unbranched hydrocarbons.

The values of the **Tarasov functions** are given in Appendix 6.

The Tarasov equations eliminate the gap between the classical expression for the heat capacity of a monoatomic gas and the cubic Debye equation, and make it possible to calculate the heat capacities and enthalpies of substances that were previously determined by the trial and error method with the aid of a sum of the Einstein and (or) Debye functions. The nature of the relationship $C_V = \varphi(T)$ permits us to determine the structure of a compound; this is especially important for substances in the glassy state, since x-ray and electron diffraction analyses do not always give unambiguous results for them.

Tarasov also considered the calculation of the heat capacity of substances characterized by the interaction of chains and laminas.

Example 5. The heat capacity of As_2O_3 at $t = -213.0$ equals 5.839, and at -130.2 °C it equals 13.80 cal/mol·K. Use these data to determine the structure of the substance.

Solution. Assume that at such a low temperature the limiting law of the form $C_V = aT^n$ holds, i.e. $\log C_V = \log a + n \log T$. We find from the equations $\log 5.839 = \log a + n \log 60.2$ and $\log 13.80 = \log a + n \log 143.0$ that $a = 19.65$ and $n = 0.994 \approx 1$ (the temperatures were converted from °C to K for the calculations). Therefore, As_2O_3 has a chain structure.

Gases. For monoatomic gases we have $C_V = \frac{3}{2} R = \text{const}$; for polyatomic gases C_V changes with the temperature as in the general case:

$$C_V = C_{\text{trans}} + C_{\text{rot}} + C_{\text{vib}} + C_{\text{el}} \qquad (3.20)$$

The component C_{trans} for any gas equals $\frac{3}{2} R$. Since the energy of rotational motion reaches its maximum value in gases (exceptions are hydrogen and deuterium at very low temperatures), then C_{rot} is calculated following the principle of equal distribution of energy. Hence for bi- and polyatomic linear molecules $C_{\text{rot}} = \frac{2}{2} R$, and for tri- and polyatomic gases $C_{\text{rot}} = \frac{3}{2} R$.

* The linear nature of the temperature dependence of the heat capacity of rubber up to 400-500 K is explained by the fact that its characteristic temperature Θ_1 is very high (3200 K).

If the principle of equal distribution of energy is also extended to intramolecular energy, i.e. to the energy of vibrational motion, it will be found that, notwithstanding experimental data, the heat capacity can only take on values that are multiples of $\frac{1}{2} R$, does not depend on the temperature, and with identical numbers of atoms does not depend on the nature of a substance. The use of quantum formulas (the Einstein equation) for calculating C_{vib} in principle eliminates these contradictions; for gases, unlike crystalline bodies, this equation coincides well with experimental results, since, owing to the great distance between the molecules, their vibrations may be considered mutually independent.

The last addend in Eq. (3.20) may be omitted, because electronic excitation requires very high temperatures.

As a result, we get the following equation (if the pressure is not great):

$$C_p = C_V + R = \frac{3}{2} R + \frac{n}{2} R + R + R \sum^{3m-(3+n)} (\beta\nu/T)^2 \frac{e^{\beta\nu/T}}{(e^{\beta\nu/T} - 1)^2} =$$

$$= \frac{5+n}{2} R + R \sum \varphi \left(\frac{\Theta}{T} \right) \qquad (3.21)$$

where m = total number of atoms in a molecule
n = number of rotational degrees of freedom
ν = frequency of vibrations characteristic of a given bond.

For gases with a linear structure of their molecules (biatomic gases, CO_2, COS, HCN, C_2H_2, CS_2, etc.), the number of addends in C_{vib} equals $3m - (3 + 2) = 3m - 5$; for other polyatomic gases we have $3m - (3 + 3) = 3m - 6$. Tables of the Einstein functions (see Appendix 5) are used to calculate the last addend in the right-hand side of Eq. (3.21).

The numerical values of Θ for various vibrational degrees of freedom (frequencies) are determined from an analysis of the spectrum of molecules or, if such data are not available, by selection from empirically determined temperature dependences of the heat capacity. These values are given in Appendix 7 for selected gases.

In accurate calculations, we must take into account the possibility of excitation of the electron levels at very high temperatures, and also the possibility of one set of groups rotating relative to another one in complex molecules (see Chap. 15).

Liquids. The theory of the heat capacity of a liquid is still in its adolescent stage owing to the lack of a fully developed theory of the liquid state. Experimental data show that the heat capacity of a liquid usually exceeds that of gases (see also pp. 71-72).

Interpolation Equations. The temperature dependence of C_p found in various ways is generally expressed by empirical equations of the kind

$$C_p = a + bT + cT^2 + \ldots \qquad (3.22)$$

where a, b and c are constants characteristic of a given substance (the number of terms depends on the required degree of accuracy and the value of the temperature interval).

In recent years, different kinds of equations have come into favour, in particular

$$C_p = a + bT + \frac{c'}{T^2} \qquad (3.23)$$

Table 4 and Appendix 2 give a summary of the equations $C_p = \varphi(T)$ for selected substances.

Table 4. **Values of Coefficients of Eqs. (3.22) and (3.23) ***

Substance	a	$b \times 10^3$	$c' \times 10^{-5}$	$c \times 10^6$	Temperature interval, K	Probable error, %
C (diamond)	2.162	3.059	−1.303	—	273-1313	3
C (graphite)	2.673	2.617	−1.169	—	273-1373	2
	1.1	4.8	—	−1.2	—	—
CH_4	5.34	11.5	—	—	273-1200	2
CO	6.60	1.20	—	—	273-2500	2
CO_2	6.369	10.100	—	−3.405	300-1500	2.07**
H_2	6.62	0.81	—	—	273-2500	2
	6.88	0.066	—	0.279	—	—
H_2O(g)	8.22	0.15	—	1.34	300-2500	1.5
NH_3	5.92	8.965	—	−1.764	—	—
	8.04	0.7	—	5.1	—	—
NO	8.05	0.233	—	1.563	300-5000	2
N_2	6.30	1.819	—	−0.345	—	—
O_2	8.27	0.258	−1.877	—	273-5000	1.5
	6.26	2.746	—	−0.770	—	—
SO_2	8.12	6.828	—	−2.103	—	—
SO_3(g)	3.603	36.310	—	$-28.828+8.649\times\times 10^{-9}T^3$	—	—

* See also Appendix 2.
** The maximum error.

In the general case, Eq. (3.23) gives a more accurate temperature dependence of C_p for high temperatures (especially for crystalline substances whose heat capacity at room temperature is lower

than the value corresponding to the law of equal distribution of energy). Indeed, since the contribution of the third term in Eq. (3.23) to the total sum at higher temperatures diminishes, while $c' < 0$, in accordance with experimental data the temperature dependence of the heat capacity becomes almost linear. Conversely, at comparatively low temperatures c'/T^2 grows, and in accordance with experimental data this dependence becomes curvilinear. Consequently, a small extrapolation beyond the limits of the recommended temperature interval in the direction of either higher or lower temperatures does not cause a large error. When using Eq. (3.22), even a small extrapolation may lead to considerable errors, since at high temperatures the part played by the quantity cT^2 becomes so great that this may lead either to overstated results, or (if $c < 0$) to the appearance of a maximum without physical meaning.

When extrapolating the equations beyond the recommended temperature intervals, one should also bear in mind that a phase transition may occur when a substance is heated, cooled, or decomposes at high temperatures.

In addition, although up to 200-300 °C the empirical equations proposed by various authors satisfactorily reproduce the experimental data and coincide with one another, for temperatures of 1000 to 1500 °C the discrepancies reach 10%, and for very high temperatures even several scores of per cent.

The constant a in the equations $C_p = \varphi(T)$ is not the heat capacity of a substance at $T = 0$ [we are naturally speaking of Eq. (3.22), since the quantity C_p calculated by Eq. (3.23) will be negative for low temperatures], but merely an *extrapolation* constant (see Fig. 11). The most widespread three-member equations $C_p = \varphi(T)$ are true with an average error of from 1 to 3% for temperatures ranging from 0 to 1000-2000 °C (if no allotropic changes occur within this interval).

Most of the equations expressing the temperature dependence of C_p in present use for gases were found on the basis of spectroscopic data. Thus, strictly speaking, they relate to the condition $p \to 0$, i.e. to ideal gases, and are highly accurate when applied to them. It should be mentioned in passing that the difference between $C_{p=0}$ and $C_{p=1}$ is considerable only for low temperatures; at high temperatures it is, as a rule, only a fraction of a per cent. With a certain approximation, the equation $C_p = \varphi(T)$ can also be applied for moderate pressures (far from condensation even up to p = 5-10 atm). At high pressures, the change of C_p with p already becomes appreciable, and within a certain interval of pressures and temperatures — very high (see Fig. 35, p. 181 and Fig. 44, p. 198).

To find an equation on the basis of the temperature dependence of C_p, it is possible, for example, to use the **method of least squares.**

Distinguished by its simplicity, this method is often used to process experimental data. For this reason, we shall summarize it in greater detail as applied to the given case.

Since experimental data are not absolutely accurate (they always contain constant, systematic and random errors), it is necessary to find the relationship between the function (heat capacity in this case) and the argument (temperature) containing the minimum errors. This means, as the theory of probability proves, that it is necessary to choose coefficients in the equation $y = \varphi(x)$ such that the sum of the squares of the differences between the calculated and observed values of the function will be the least.

Consequently, in this case the error will be minimum when the expression

$$\Sigma\{(C_p)_i - [\varphi(T)]_i\}^2$$

is minimum. If, for example, we take an equation of the form $C_p = a + bT$, then, denoting the difference $(C_p)_i - [\varphi(T)]_i$ by Δ_i, we get

$$\Delta_i = (C_p)_i - (a + bT_i)$$

and

$$\Sigma[(C_p)_i - (a + bT_i)]^2 = \Sigma(\Delta_i)^2 = \varphi(a, b)$$

A function of many variables is minimum if its partial derivatives equal zero. Hence

$$\left[\frac{\partial\varphi(a, b)}{\partial a}\right]_b = \Sigma 2[(C_p)_i - a - bT_i](-1) = 0$$

$$\left[\frac{\partial\varphi(a, b)}{\partial b}\right]_a = \Sigma 2[(C_p)_i - a - bT_i](-T_i) = 0$$

We thus get a system of two equations with two unknowns:

$$\Sigma(C_p)_i - na - b\Sigma T_i = 0$$

and

$$\Sigma(C_p)_i T_i - a\Sigma T_i - b\Sigma T_i^2 = 0$$

whence we determine a and b (in the upper equation n is the number of experimental points).

Similarly, if we have the relationship $C_p = a + bT + cT^2$ or $C_p = a + bT + c'T^{-2}$, we find a, b and c (or a, b and c') by solving a system of three equations with three unknowns.

The **method of mean values** is simpler, but less accurate: after the values of Δ_i are written, they are summed into groups with an equal number of addends (the number of groups is determined by the number of coefficients), and the equations thus obtained are solved relative to their coefficients.

When the values of the function are known for equally spaced values of the argument (for example C_p has been determined at intervals of 10 or 100 kelvins), it is good to use the method of P. Chebyshev (see, for example, [B114]) to select the coefficients of an equation.

3.4.3. Certain Laws

Crystals. The molar heat capacity may be considered equal to the sum of the atomic heat capacities; the latter, in turn, are assumed to be the same for elements and are taken equal to 6.2 (the **Dulong and Petit law**). For the light elements, however, this law is unsatisfactory, and the data given in Fig. 13 should be used even for approximate calculations. It is also possible to use a law according to which the molar heat capacity of chemically similar crystalline compounds is approximately identical (if a substance forms several allotropic modifications, the densest of them has a lower heat capacity).

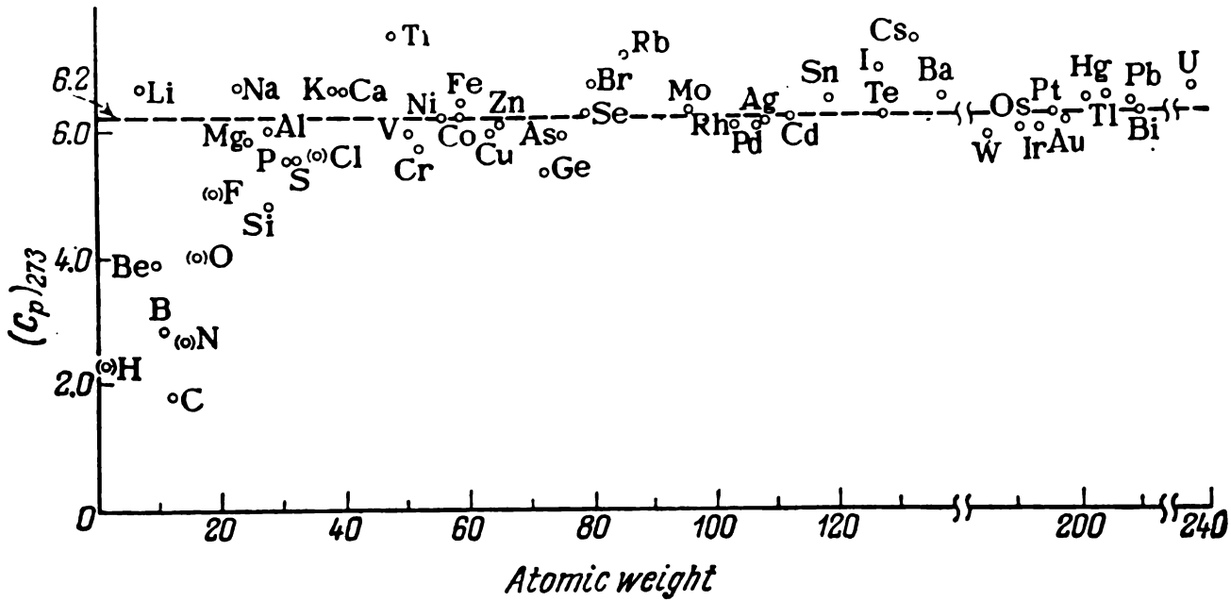


Fig. 13. Heat capacities of selected elements.
Checking of the Dulong and Petit law;
$C_V \approx 6.2$ cal/mol·K

Gases. The heat capacity C_p can be calculated on the basis of the **method of thermal corrections** similar to that considered on p. 55. The data needed for calculating the coefficients *a*, *b* and *c* of Eq. (3.22) are given in the tables of Appendix 3.

Liquids. The heat capacity of liquids is usually somewhat greater than that of crystalline substances. The change in the heat capacity with temperature may often be disregarded, because heating (cooling) generally occurs within a comparatively small temperature interval. The specific heat capacity of liquids may be considered approximately equal to 0.4-0.6 cal/g·K. Exceptions among the investigated

substances are H_2O and NH_3 (about 1 cal/g·K), Hg (about 0.03), $SiCl_4$ (about 0.2), and the halogen derivatives of hydrocarbons of the fatty and aromatic series (0.15-0.35). For similar substances, the interval of the values of the specific heat capacity of liquids can apparently be decreased. Thus, for 30 saturated hydrocarbons having from 5 to 13 carbon atoms, the average value of the specific heat capacity at 0 °C was found to equal 0.505 cal/g·K with a mean error of 2.4% and a maximum error of 6%. For 20 saturated hydrocarbons at 25 °C, the same quantity is equal to 0.525 (the errors are 1.5 and 4.7%, respectively).

In the equation $C_p = a + bt$, the quantity b/a is approximately the same for various substances, and for the majority of organic compounds is close to 0.0022.

Without having any direct or indirect data for determining the specific heat capacity of alloys, slags, glass and solutions, we can use the approximate formula

$$c \approx \frac{g_1c_1 + g_2c_2 + \cdots}{100}$$

where g_1, g_2, ... = weight per cents of the corresponding constituent parts of the mixture

c_1, c_2, ... = their specific heat capacities.

When the heats of mixing (solution) are considerable, this equation gives an overstated result.

Comparative Calculation of Heat Capacity. The heat capacity of various substances can be calculated approximately by the methods of comparative calculation [B45], particularly the first of them, i.e. the relationship

$$(C_p)_{II} \approx A(C_p)_I + B \qquad (3.24)$$

Thus, the approximate equation $(C_p)_{NaHal} \approx 1.40(C_p)_{KHal} - 5.4$ describes the relationship between the isobaric heat capacities of potassium and sodium halides at 25 °C with a mean error of 0.1 cal/mol·K.

It is also possible to use the fourth method of comparative calculation in the form of the relationship

$$(C_p)_N \approx A(C_p)_M + B \qquad (3.25)$$

which compares the heat capacities of two substances, analogues, at equal temperatures. Two examples of expression (3.25) are shown in Fig. 14 for standard heat capacities. * Quite often in expression (3.25) we have $B \approx 0$. Here expression (2.16) follows from (3.25).

* Inspection of straight line *2* shows the similarity of carbon monoxide and nitric oxide — the points are on a straight line that almost coincides with the bisector of the quadrant.

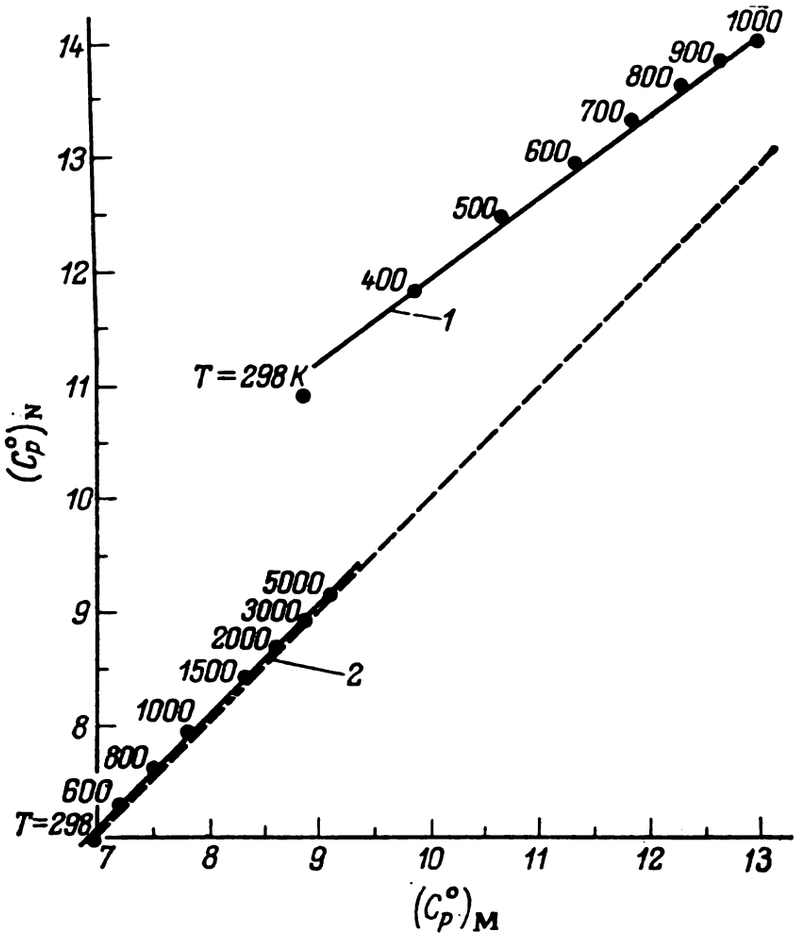


Fig. 14. Relationship between standard heat capacities of :
1—CO_2 and CS_2; *2*—N_2 and CO

3.5. TEMPERATURE DEPENDENCE OF HEAT EFFECT

3.5.1. Kirchhoff Equation

A change in a system due to a simultaneous change in T and p can be represented in the form of two processes, one of which is due only to a change in temperature, and the other only to a change in pressure. Consequently, we can study the dependence of ΔH of a reaction on each of these factors separately. It has already been noted that the change in ΔH with pressure is considerable only at very high pressures (see also pp. 185-186), and the question of the influence of temperature on the heat effect of a reaction has much more practical importance.

The change in the heat effect of a reaction with a change in temperature in accordance with Eq. (3.11) is expressed by the **Kirchhoff equation** (1858)

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_p = \Delta\left(\frac{\partial H}{\partial T}\right)_p = \Sigma(C_p)_{pr} - \Sigma(C_p)_r = \Delta C_p \qquad (3.26)$$

where ΔC_p is the difference between the molar heat capacities of the reagents with account taken of their stoichiometric coefficients.

Equation (3.26) strictly holds only on the condition that the pressure over each of the components at the necessary temperature will be the same as at the given temperature.

It follows from Eq. (3.26) that the sensitivity of ΔH to a change in temperature is determined by the absolute value of ΔC_p, while the sign of the temperature coefficient of the heat effect is determined by the sign of ΔC_p; when $\Delta C_p > 0$, the heat effect of a reaction grows with increasing temperature, when $\Delta C_p < 0$, it diminishes, and when $\Delta C_p = 0$, it does not depend on the temperature. We must not forget the fact that the sign of ΔC_p is also connected with the choice of the sign of the heat effects. This can be seen from the following example:

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \frac{(-21\,000) - (-20\,000)}{1100 - 1000} = -10$$

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \frac{21\,000 - 20\,000}{1100 - 1000} = 10$$

The nature of the change in ΔH with a change in temperature is due to the nature of the change in ΔC_p with the temperature. Figure 15 schematically shows all the possible cases except for those

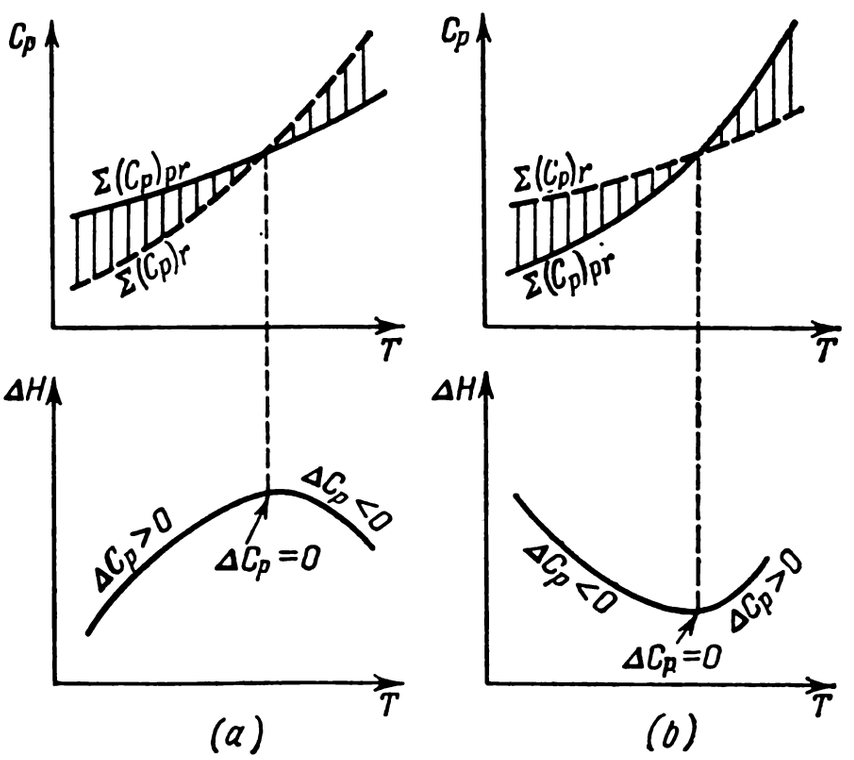


Fig. 15. Schematic diagrams of temperature dependences of C_p (ΔC_p) and ΔH

when the curves $\Sigma(C_p)_r$ and $\Sigma(C_p)_{pr}$ are equidistant, i.e. when ΔH is a linear function of the temperature. An extremum is relatively rarely observed on the curves of ΔH against T, since the tempera-

ture intervals are usually not very great. The very possibility of the appearance of an extremum, however, is an indication that considerable extrapolation of the temperature dependence of the heat effect beyond the limits of the experimental data or the guaranteed accuracy of the relevant formulas should never be tolerated.

Figure 16 shows the temperature dependence of $\Delta H°$ for several reactions. The values of $-a\Delta H°$ are given for some of them for

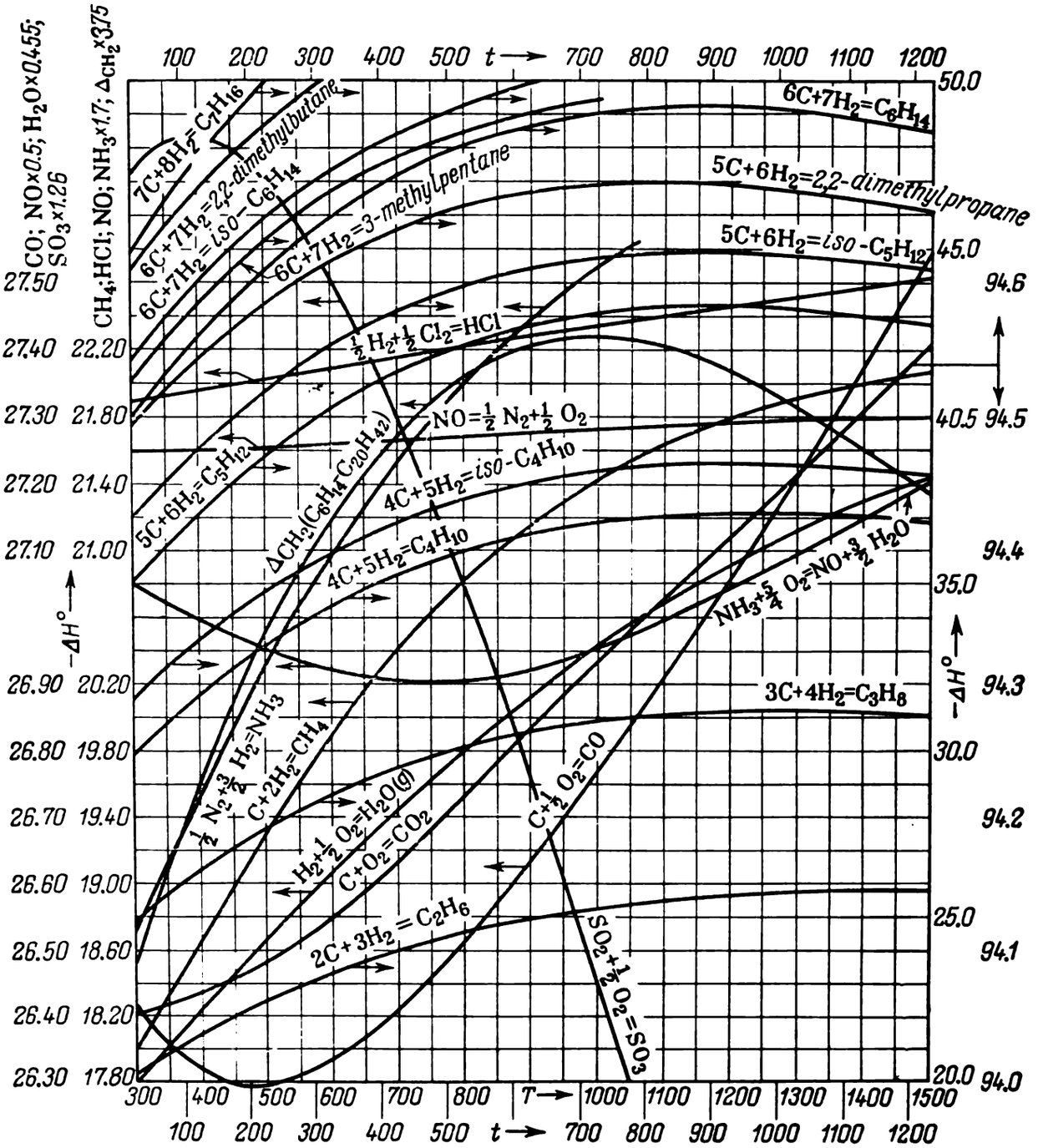


Fig. 16. Temperature dependence of heat effect for selected reactions.

To determine $\Delta H°$ of formation of CO, H_2O, CH_4, HCl, NO, NH_3 and NO (from NH_3), the value read off on the axis of ordinates opposite the corresponding compounds should be divided by the coefficient indicated in the top left-hand corner. The same applies to the gaseous hydrocarbons (from C_6H_{14} to $C_{20}H_{42}$), for which the values of Δ_{CH_2} equal to the increment of $\Delta H°$ of formation upon transition from the given homologue to the adjacent one are given

purposes of convenience and greater accuracy. Here a is a coefficient which the quantities given in the figure should be divided by to obtain the value of $-\Delta H°$. For example, for the reaction $H_2 + \frac{1}{2} O_2 = H_2O(g)$ at $T = 1200$ we have $-\Delta H° = 27\,075/0.455$, i.e. $\Delta H°_{1200} = -59\,510$ cal/mol.

Calculations using Eq. (3.26) require that we know the values of the heat effect of a given reaction at any temperature, and also the temperature dependence of the heat capacity for all the reactants. The calculations can be performed either graphically or analytically.

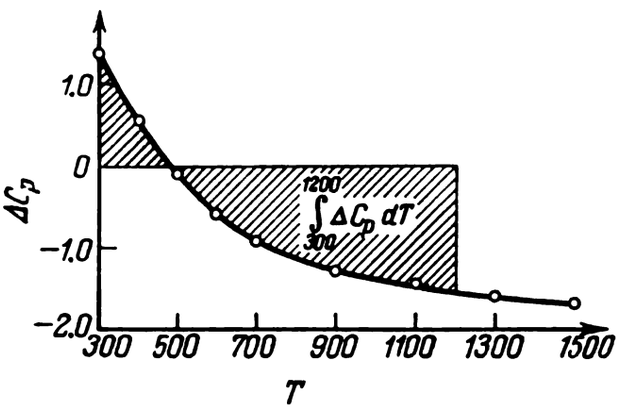


Fig. 17. Dependence of the algebraic sum of the heat capacities of the reagents on the temperature for the reaction

$$C\ (graphite) + \frac{1}{2} O_2(g) = CO(g).$$

To the graphical calculation of the heat effects of reactions. (See Example 6)

In the first case, a chart is plotted in the coordinates $\Delta C_p = \varphi(T)$ [Fig. 17, $\Delta C_p = (C_p)_{CO} - (C_p)_C - \frac{1}{2}(C_p)_{O_2}$]; hence by Eq. (3.26) we have

$$\Delta H^{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p dT \quad (3.27)$$

The second term of the right-hand side of this equation is shown in Fig. 17 by the shaded area.*

The graphical method of calculation is especially convenient when an algebraic expression for $\Delta C_p = \varphi(T)$ is unknown or is selected with difficulty.

Example 6. Find the heat effect of the reaction

$$C\ (graphite) + \frac{1}{2} O_2 = CO$$

* Graphical integration is performed either with the aid of a planimeter or by counting the number of squares on graph paper. In the latter case, it is good to divide the entire area with vertical lines into separate smaller areas that can be assumed to be trapezoids. Before the value of the area corresponding to the value of the integral is inserted into Eq. (3.27), it must be expressed in units of the scale. If the drawing is made on paper of uniform density, then the area being determined as well as an area corresponding to the unit of the scale can be cut out and weighed. Division of the first weight by the second gives the necessary result.

at $T = 1200$ if $\Delta H = -26\,420$ and the heat capacities of the reagents are:

T	300	400	500	600	700	900	1100	1300	1500
C_p C	2.08	2.85	3.50	4.03	4.43	4.98	5.27	5.57	5.76
C_p O_2	7.02	7.19	7.43	7.67	7.88	8.21	8.44	8.61	8.74
C_p CO	6.96	7.01	7.12	7.28	7.45	7.79	8.06	8.26	8.42

Solution. Calculations of the value of $\Delta C_p = (C_p)_{CO} - (C_p)_C - \frac{1}{2}(C_p)_{O_2}$ yield

T	300	400	500	600	700	900	1100	1300	1500
ΔC_p	1.38	0.56	−0.09	−0.59	−0.92	−1.30	−1.43	−1.61	−1.71

After plotting ΔC_p against T (see Fig. 17) and determining the area confined by the curve $\Delta C_p = \varphi(T)$, the perpendiculars erected from the temperatures $T_1 = 300$ and $T_2 = 1200$, and the axis of abscissas, in accordance with Eq. (3.27), we have

$$\Delta H^\circ_{1200} = \Delta H^\circ_{300} + \int_{300}^{1200} \Delta C_p \, dT \approx -26\,420 + (-650) = -27\,070$$

(the area above the axis of abscissas is positive, and under it is negative). Note that when $T \approx 490$ K, the value of ΔH° passes through a minimum (in its absolute value) and at $T \approx 700$ K again becomes equal to ΔH°_{300}. These conclusions directly follow from Fig. 17 and are confirmed by Fig. 16.

3.5.2. Equation $\Delta H = \varphi(T)$ in Its Final Form

Accurate Solution. It follows from Eqs. (3.22) and (3.23) that

$$\Delta C_p = \Delta a + \Delta b T + \Delta c T^2 + \Delta c' T^{-2} \qquad (3.28)$$

Introducing Eq. (3.28) into Eq. (3.26) and integrating, we get the temperature dependence of ΔH in its final form:

$$\Delta H = \Delta H_0 + \Delta a T + \frac{1}{2}\Delta b T^2 + \frac{1}{3}\Delta c T^3 - \Delta c' T^{-1} \qquad (3.29)$$

It is obvious that if $C_p = \varphi(T)$ for all the reagents is expressed by Eq. (3.22) or (3.23), then the relationship $\Delta H = \varphi(T)$ will differ from Eq. (3.29) in the absence of the term $-\Delta c' T^{-1}$ or correspondingly of the term $\frac{1}{3}\Delta c T^3$. A mathematical analysis of Eq. (3.29) gives us grounds to consider the quantity ΔH_0 to be the heat effect of a reaction at absolute zero, but the path followed by the curve

in the region close to absolute zero changes. Therefore, the constant of integration of ΔH_0 is only an *extrapolation* constant (similar to the quantities a and Δa), while Eq. (3.29) is an interpolation one. It is used not only to find ΔH for a reaction at various temperatures, but, most importantly, to also determine how the temperature affects chemical equilibrium (see Chap. 13).

Should a phase transition (melting, vaporization or sublimation) occur within the given temperature interval, then the heats of the corresponding transformations must be included in the calculations. We must also keep in mind the change in the temperature dependence of the heat capacity of the substance that has undergone a phase transition. Thus, if a phase transition of one of the reagents occurs at T_{tr}, then the Kirchhoff equation acquires the form

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_{tr}} \Delta C_p \, dT + \Delta H_{tr} + \int_{T_{tr}}^{T_2} \Delta C'_p \, dT \qquad (3.30)$$

where ΔH_{tr} is subtracted when a reactant undergoes a phase transition and is added when a product undergoes one. The relationship between Eqs. (3.30) and (3.13) is obvious.

When calculating heat effects, it should be borne in mind that a considerable graphical extrapolation of the quantities ΔH is not reliable: the different rate of change of C_p with a change in temperature for different substances may result in a change in the sign of ΔC_p, and, consequently, in accordance with Eq. (3.26) an extremum may appear on the curve $\Delta H = \varphi(T)$.

A considerable analytical extrapolation is also without grounds: even the most accurate equations $C_p = \varphi(T)$ may give not only a great deviation from experimental data, but also maxima that actually do not exist. The inaccuracy of the equation $C_p = \varphi(T)$ within a given temperature region may also be a source of error. Hence the total error in calculating ΔC_p may become considerable.

The availability of data on the standard heat effects of formation and combustion of various substances considerably simplifies calculations. Using the values of ΔH°_{298} taken directly from the relevant tables (or found by combining tabulated data) and the equations $C_p = \varphi(T)$ needed to determine Δa, Δb, ..., we compute the constant of integration of ΔH°_0 by Eq. (3.29), which makes it possible to find ΔH° for any temperature.

It is not necessary to calculate ΔH_0 if we take a definite integral. In this case instead of Eq. (3.29) we get

$$\Delta H_{T_2} = \Delta H_{T_1} + \Delta a(T_2 - T_1) + \frac{1}{2}\Delta b\,(T_2^2 - T_1^2) + \ldots \qquad (3.31)$$

This equation can also be derived using the temperature dependence of the enthalpy of each reagent

$$H_{T_2} = H_{T_1} + \int_{T_1}^{T_2} C_p \, dT \tag{3.32}$$

When values of $H_T^\circ - H_{298}^\circ$, $H_T^\circ - H_0^\circ$ and $H_{298}^\circ - H_0^\circ$ are available (they are usually given in tables, and less frequently are presented in an analytical form), we can use various alternatives of the relationship $\Delta H^\circ = \varphi(T)$, including the following:

$$\Delta H_T^\circ = \Delta H_{298}^\circ + \Delta(H_T^\circ - H_{298}^\circ) \tag{3.33}$$

$$\Delta H_T^\circ = \Delta H_{298}^\circ + \Delta(H_T^\circ - H_0^\circ) - \Delta(H_{298}^\circ - H_0^\circ) \tag{3.34}$$

and

$$\Delta H_T^\circ = \Delta H_0^\circ + \Delta(H_T^\circ - H_0^\circ) \tag{3.35}$$

When considering the influence of the temperature on chemical equilibrium (see Chap. 13), it is convenient to use for each reagent the quantities $(H_T^\circ - H_{T_1}^\circ)/T$ (here T_1 is the temperature adopted as the basic one). The function $(H_T^\circ - H_{T_1}^\circ)/RT$ is still more convenient, since it depends neither on the amount of substance nor on the units of measurement. It is quite obvious that

$$\Delta\left(\frac{H_T^\circ - H_{T_1}^\circ}{T}\right) = \sum\left(\frac{H_T^\circ - H_{T_1}^\circ}{T}\right)_{pr} - \sum\left(\frac{H_T^\circ - H_{T_1}^\circ}{T}\right)_{r} \tag{3.36}$$

Generally 0 K is taken as the basic temperature (less often 298.15 K). The transition from one basic temperature to another is described by the equation

$$\frac{H_T^\circ - H_0^\circ}{T} = \frac{H_T^\circ - H_{298}^\circ}{T} + \frac{H_{298}^\circ - H_0^\circ}{T}$$

The calculation of ΔH_T° is also treated on p. 503 and pp. 592 et seq.

Example 7. Find the equation $\Delta H^\circ = \varphi(T)$ and compute ΔH_{1000}° for the reaction $CH_4 = C + 2H_2$ if $\Delta H_{298}^\circ = 17\,880$ (see Table 1) and

$$(C_p)_C = 2.673 + 2.617 \times 10^{-3}T - 1.169 \times 10^5 T^{-2}$$

$$(C_p)_{H_2} = 6.62 + 0.81 \times 10^{-3}T$$

$$(C_p)_{CH_4} = 5.34 + 11.5 \times 10^{-3}T$$

(see Table 4).

Solution. Using the data given above, we find $\Delta a = a_C + 2a_{H_2} - a_{CH_4} = 10.573$, $\Delta b = -7.263 \times 10^{-3}$, and $\Delta c' = -1.169 \times 10^5$. Hence by Eq. (3.29) we have

$$\Delta H^\circ = \Delta H_0^\circ + 10.573T + \frac{1}{2}(-7.263 \times 10^{-3})T^2 + 1.169 \times 10^5 T^{-1}$$

Using the value of ΔH°_{298}, we compute $\Delta H_0^\circ = 14\,658$ according to the derived equation. We finally get

$$\Delta H^\circ = 14\,658 + 10.573T - 3.632 \times 10^{-3}T^2 + 1.169 \times 10^5 T^{-1}$$ and

$$\Delta H^\circ_{1000} = 21\,716 \text{ cal/mol}$$

[the deviation from the value of ΔH°_{1000} in Fig. 16 is 1.5%, i.e. within the limits of the error of the equations $C_p = \varphi(T)$].

Example 8. Use the equations

$$(C_p)_C = 1.1 + 4.8 \times 10^{-3}T - 1.2 \times 10^{-6}T^2$$

$$(C_p)_{O_2} = 6.26 + 2.746 \times 10^{-3}T - 0.770 \times 10^{-6}T^2$$

$$(C_p)_{CO} = 6.60 + 1.20 \times 10^{-3}T$$

to find the temperature interval within which the heat effect of the reaction $C + \frac{1}{2}O_2 = CO$ does not depend on the temperature.

Solution. By the equations $C_p = \varphi(T)$, we find

$$\Delta C_p = (C_p)_{CO} - (C_p)_C - \frac{1}{2}(C_p)_{O_2} = 2.37 - 4.973 \times 10^{-3}T +$$

$$+ 1.585 \times 10^{-6}T^2$$

In accordance with Eq. (3.26), the condition where ΔH° does not depend on the temperature is the equation $\Delta C_p = 0$, i.e. $2.37 - 4.973 \times 10^{-3}T + 1.585 \times 10^{-6}T^2 = 0$, whence $T \approx 586$.

Since the terms of the equation $\Delta C_p = \varphi(T)$ containing T are negative, then at $T > 586$ we have $\Delta C_p < 0$, i.e. at this temperature ΔH° passes through a minimum. The failure of the results of the calculations to coincide with the exact value (see Figs. 15 and 16) is explained by the error in the equations $C_p = \varphi(T)$ on which the calculations are based. The minimum on the curve $\Delta H^\circ = \varphi(T)$ in Fig. 16 actually corresponds to the maximum value of ΔH°, since in the process being considered $\Delta H^\circ < 0$ (see also the solution of Example 6).

Example 9. Using the data given in Fig. 16, find ΔH for the reaction $C + CO_2 = 2CO$ within the interval of 400 to 1400 °C for steps of 200 K.

Solution. Multiplying by two the values of ΔH_T° given in Fig. 16 for the reaction $C + \frac{1}{2}O_2 = CO$ at the relevant temperatures and

subtracting from them the values of ΔH_T° for the reaction $C + O_2 = CO_2$, according to Hess's law we get the following results for the reaction $C + CO_2 = 2CO$:

T	400	600	800	1 000	1 200	1 400
ΔH°	41 430	41 460	41 180	40 780	40 300	39 750

Calculations for higher temperatures [according to the equation $\Delta H^\circ = \varphi(T)$] cannot give reliable results, because the equation $C_p = \varphi(T)$ for graphite is sufficiently accurate (an error of about 2%) only for $T = 1373$ (see Table 4).

Approximate Solutions. Let us now consider approximate solutions of the temperature dependence of the heat effect.

1. The contribution of the last term in Eqs. (3.22) and (3.23) at different temperatures is not the same. As a result, the transition from Eq. (3.29) to the equation

$$\Delta H = \Delta H_0 + \Delta a T + \frac{1}{2}\Delta b T^2 \qquad (3.37)$$

which assumes a linear dependence of C_p on T for all reagents may lead to a considerable error in the calculations. Consequently, when transferring to an approximate equation, it is better to proceed from Eq. (3.22) for low temperatures and from Eq. (3.23) for high ones, since it is exactly in these cases that the last addend of the above equations becomes small.

2. For gases within a comparatively narrow temperature interval, and for solids and liquids within a sufficiently broad one, we may consider that $\Delta C_p \approx \text{const}$, i.e. use the linear equation

$$\Delta H = \Delta H_0 + \Delta a T \qquad (3.38)$$

it being good practice, although this sometimes results in a certain loss of accuracy, to assume that $\Delta a = (\Delta C_p)_{298}$, because the values of $(C_p)_{298}$ for the majority of the most important substances are known with a high degree of authenticity (see Appendix 2).

3. If the value of ΔH_{298} is very great (of the order of magnitude of scores and hundreds of thousands of calories), then in a number of cases it may be assumed that $\Delta C_p \approx 0$, i.e. it may be considered that $\Delta H \approx \Delta H_{298} = \text{const}$, since often the change in ΔH with temperature does not exceed the error introduced by the equations $C_p = \varphi(T)$ (see Table 4 and Fig. 16) and by the quantity ΔH_{298}. The errors connected with the assumption that $\Delta H = \text{const}$ may be much smaller than the inaccuracy involved in extrapolation to very high temperatures of the complete equation $\Delta H = \varphi(T)$ obtained on the basis of low-temperature values of the heat capac-

ities. Consequently, the heat of combustion of organic compounds (especially of polyatomic ones) may be considered actually unchangeable with a change in temperature.

The assumption that $\Delta H = \text{const}$ gives a comparatively small error, especially for reactions between solids, since in many cases the heat capacity of a compound is close to the sum of the atomic heat capacities. Generally speaking, the assumption that $\Delta C_p \approx 0$ ($\Delta H \approx \text{const}$) for the formation of comparatively simple molecules leads to a small error. Thus, for 14 gases ($COCl_2$, HCN, CO, CO_2, C_2N_2, HCl, HF, H_2O, H_2O_2, NH_3, NO, NO_2, N_2O and O_3) the mean discrepancy between the values of ΔH°_{298} and ΔH°_{1000} is only 0.35 kcal/mol (see also the solution of Example 9).

4. The calculations give sufficiently satisfactory results even for a broad temperature interval if we assume the values of C_p equal to the mean heat capacities within the given interval, i.e. if we pass over from Eq. (3.27) to the equation

$$\Delta H_{T_2} = \Delta H_{T_1} + (\Delta C_p)_{(T_1 \text{ to } T_2)} (T_2 - T_1) \qquad (3.39)$$

This considerably simplifies calculations and is especially convenient when tables of the values of mean heat capacities are available.

5. To assess the relationship $\Delta H = \varphi(T)$, we can also use comparative methods, in particular the approximate relationship

$$\Delta H_N \approx A \Delta H_M + B \qquad (3.40)$$

where the heats of similar reactions (for example, the heats of formation of related substances, Fig. 18) are compared for identical temperatures. A similar relationship

$$(\Delta C_p)_N \approx A (\Delta C_p)_M + B \qquad (3.41)$$

can be used to assess the values of ΔC_p needed to calculate the temperature dependence of ΔH (Fig. 19).

Example 10. Use Eq. (3.39) to calculate ΔH°_{1000} for the cracking of methane and compare the result obtained with that found in solving Example 7. Take the values of the mean heat capacity of the reagents for the interval from 298.2 to 1000 K.

Solution. In accordance with the equations of the temperature dependence of C_p (see Table 4), by Eq. (3.9) we get expressions for the mean heat capacity:

$$(C_p)_C = a_C + \frac{1}{2} b_C (T_1 + T_2) + \frac{c'_C}{T_1 T_2} = 3.98$$

$$(C_p)_{H_2} = 7.15 \text{ and } (C_p)_{CH_4} = 12.81 \text{ cal/mol·K}$$

whence $(\Delta C_p)_{(T_1 \text{ to } T_2)} = 5.47$ and by Eq. (3.39) we have $\Delta H^\circ_{1000} - 17\,880 = 5.47(1000 - 298.2)$, i.e. $\Delta H^\circ_{1000} = 21\,719$, which coincides with the result of the exact solution.

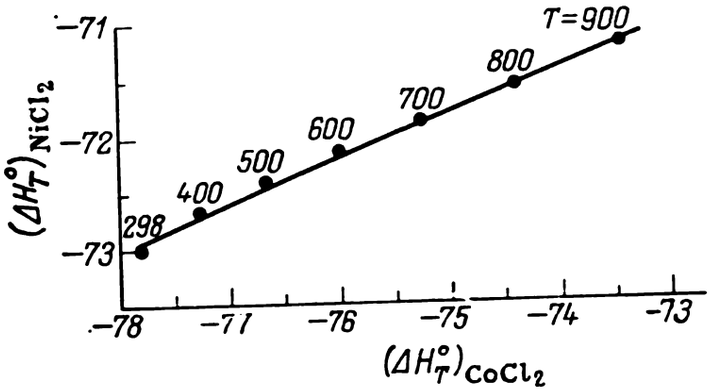


Fig. 18. Relationship between the heats of formation of cobalt and nickel chlorides

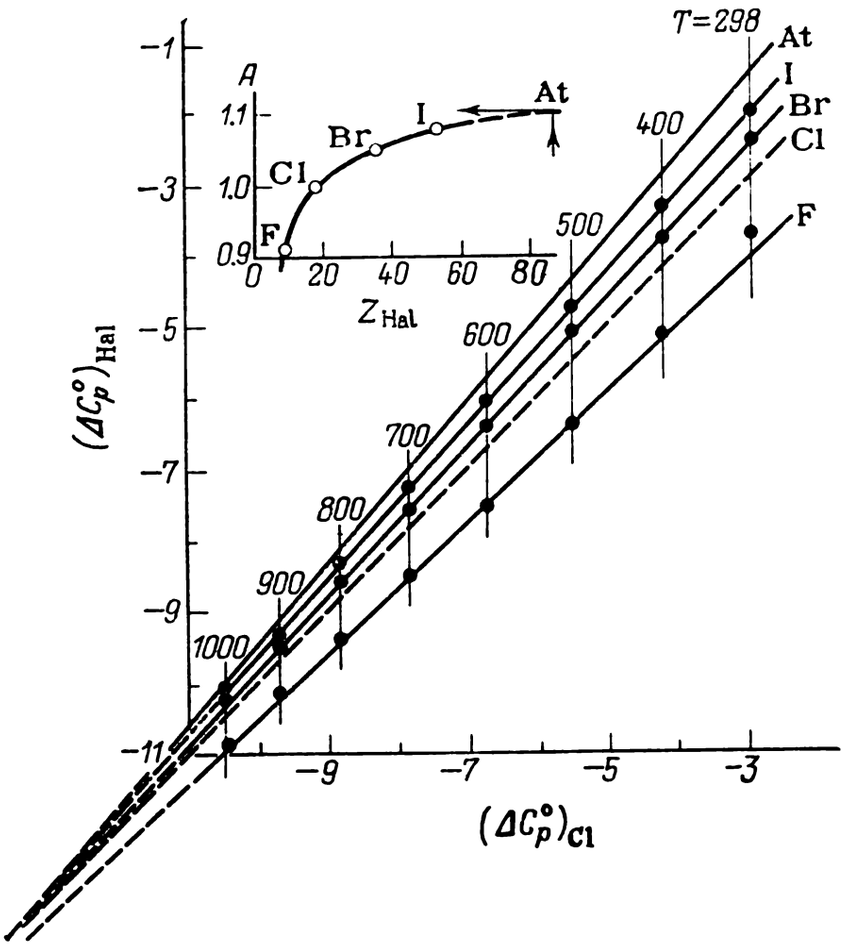


Fig. 19. Relationship between the change in the heat capacity in the reactions $C_2H_6(g) + \frac{1}{2} Hal_2(g) = C_2H_5Hal(g)$.

The dependence of the coefficient A of Eq. (3.41) on the atomic number Z_{Hal} of the halogens is shown in the top left-hand corner of the chart. It permits one to assess the relationship $\Delta C_p^\circ = \varphi(T)$ for a reaction with At_2 without any experimental data

If we assume the value of $\Delta C_p = (\Delta C_p)_{298}$, then by Eq. (3.38) in accordance with the data of Appendix 2 we get $\Delta H_{1000}^\circ - 17\,880 = 7.31(1000 - 298.2)$, whence $\Delta H_{1000}^\circ = 23\,010$ cal/mol, which

differs from the exact value by 7.4%. Such a big error is due to the considerable magnitude of the temperature interval.

3.5.3. Heat Balance

We have considered a very simple case of calculating ΔH. In practice, the drawing up of a heat balance is frequently made more complicated by the non-adiabatic nature of a process, the difference in the temperatures of the reagents, the failure to observe stoichiometric relationships, the presence of inert gases and by an incomplete course of a process.* In this connection we shall consider two examples.

Assume that $T_r \neq T_{pr}$ (Fig. 20). Hence the process can be considered as proceeding in several stages: the reaction proceeds at T_r

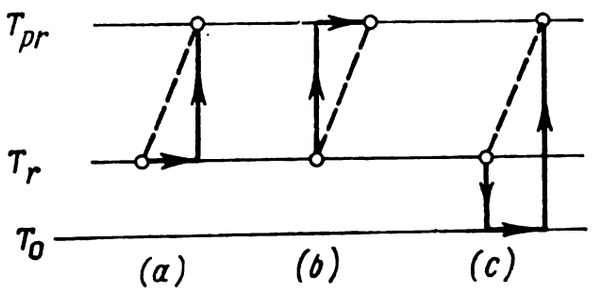


Fig. 20. Possible paths of a real process.
Illustrating the drawing up of a heat balance

and then the products are heated to T_{pr} (Fig. 20*a*), or first the reactants are heated, after which the process is conducted (Fig. 20*b*). Another variant is possible: the reactants are cooled (heated) to a certain temperature T_0 at which the reaction is conducted, and then the products are heated (cooled) to T_{pr} (Fig. 20*c*). Although the last method is more complicated than the preceding ones, it is preferable if T_0 is taken equal to 298.15 K. The calculations are simplified if the mean heat capacities of all the reagents are known within the interval of temperatures being calculated. For case (*c*) we obviously have

$$\sum_r n_i \left(\int_{T_r}^{T_0} C_{p_i} dT + \Delta H_{tr} \right)_i + \xi n_{bas} \Delta H_{T_0} + \\ + \sum_{pr} m_i \left(\int_{T_0}^{T_{pr}} C_{p_i} dT + \Delta H_{tr} \right)_i = Q \qquad (3.42)$$

* In addition, at high temperatures we must also take into account possible dissociation of some substances. For this purpose, however, the influence of temperature on chemical equilibrium must be taken into consideration, which is treated in Chapters 13 and 14.

Here the first addend is the change in enthalpy upon a transition of all the reactants (including inert gases if they are present in the initial mixture) from the temperature T_r of their entry into the reaction zone to the temperature T_0 of the beginning of counting the enthalpy; the second addend equals the heat effect of the reaction at T_0 calculated per mole of substance (the basic substance for which the calculations are being conducted) taking into account the extent of the reaction ξ; the third addend is the change in enthalpy upon heating all the substances leaving the reaction zone (the products, inert substances and the unreacted reactants). If no phase transitions occur during the change in temperature, then all the values of ΔH_{tr} will equal zero. If phase transitions do occur, then to simplify the calculations they may be related to T_0.

Equation (3.42) can be used to calculate the temperature reached upon complete adiabatic combustion of a substance (the **theoretical temperature of combustion**). In this case $Q = 0$. For explosive reactions, the quantities C_V and ΔU will enter Eq. (3.42), respectively. At $T_1 = T_2 = T_0 = T$, $\xi = 1$ and $Q = n_{bas}\Delta H_T$, Eq. (3.42) coincides with Eq. (3.27).

Example 11. In the production of ethene oxide according to the reaction

$$C_2H_4 + \frac{1}{2}O_2 = C_2H_4O(g)$$

we have $t = 280\,^\circ C$ and $p = 1$ atm. The ethene and oxygen enter the reactor at 80 °C, and the amount of oxygen used is 10% greater than the stoichiometric amount. The degree of transformation of the C_2H_4 (the extent of the reaction) equals 80%. How much heat will be needed to maintain an isothermal process if 140 kg of C_2H_4 are fed into the reactor an hour?

The values of the quantities needed for the calculations are summarized in the following table:

Substance	$(\Delta H^\circ_{298})_{form}$, cal/mol	$(C_p)_r$ (mean value)	$(C_p)_{pr}$ (mean value)	n_r	n_{pr}
C_2H_4	12 540	11.2	14.0	1.0	1.0 − 0.8 = 0.2
O_2	0	7.05	7.35	0.55	0.55 − 0.4 = 0.15
C_2H_4O	−12 580	12.3	15.5	0	0 + 0.8 = 0.8

Solution. According to Hess's law, we have $\Delta H_{298} = -12.58 - (-12.54) = -25.12$ kcal/mol of C_2H_4, i.e. $0.8 \times 25.12 = 20.10$ kcal will be liberated per mole of ethene fed into the reactor.

The enthalpy of the reactants equals

$$(n_r)_{C_2H_4} \int_{298}^{353} (C_p)_{C_2H_4}\, dT + (n_r)_{O_2} \int_{298}^{353} (C_p)_{O_2}\, dT =$$

$$= 1 \times 11.2(353 - 298) + 0.55 \times 7.05(353 - 298) = 829 \text{ cal}$$

The enthalpy of the products is

$$n_{C_2H_4O} \int_{298}^{553} (C_p)_{C_2H_4O}\, dT + (n_{pr})_{C_2H_4} \int_{298}^{553} (C_p)_{C_2H_4}\, dT +$$

$$+ (n_{pr})_{O_2} \int_{298}^{553} (C_p)_{O_2}\, dT = 0.8 \times 15.5(553 - 298) +$$

$$+ 0.2 \times 14.0(553 - 298) + 0.15 \times 7.35(553 - 298) = 41.59 \text{ cal}$$

Consequently, in accordance with Eq. (3.42), we have $0.829 + Q = -20.10 + 4.159$, whence $Q = -16.77$ kcal should be added per mole of ethene supplied to the reactor, i.e. $16.77 \times 140 \times 1000/28 = 83\,850$ kcal (28 is the molecular weight of ethene) should be removed every hour.

Chapter 4

THE SECOND LAW OF THERMODYNAMICS

4.1. CONTENT OF THE SECOND LAW

All nature's processes obey the first law of thermodynamics, but only part of the processes not contradicting the first law can be realized in practice. It only follows from the first law that the energy of an isolated system is constant. It is impossible, however, to determine the *direction* of the processes in a system. For example, it is impossible on the basis of the first law to decide whether energy is transferred from a warmer to a colder body or vice versa and to give an exact definition of temperature.

Like the first law of thermodynamics, the second cannot be derived from any general rule, but is established empirically. It makes it possible to divide all the processes allowed by the first law into spontaneous and unspontaneous under the given conditions. The formulation of the second law is often based on the impossibility of a certain process.

We shall base our further reasoning on the postulate of R. Clausius (1850) : *heat cannot pass by itself from a cold body to a hot one,* i.e. a process whose *only* result would be the transfer of heat from a body with a lower temperature to one with a higher temperature is impossible *. Such reasoning should not be considered as a purposeful limitation of the general nature of the second law; confirming the impossibility of a given process, we can easily arrive at any other formulation (all of them are set out in the text in italics).

4.1.1. The Carnot Cycle

When considering the first law, it was pointed out that there is a radical difference between heat and work. In contrast to the con-

* M. Lomonosov was the first to indicate (1747) the definite direction of nature's processes. In "Reflection on the Nature of Heat and Cold" he wrote : "...cold body *B* submerged into body *A* cannot obviously take on a greater degree of heat than that which *A* has." M. V. Lomonosov. *Polnoe sobranie sochinenii* (Collected Works), Vol. 2. Moscow, USSR Acad. of Sc. (1951). See p. 37.

version of work into heat, the reverse process is limited by definite conditions. For this reason, there is a limit even in the optimal case for the conversion of heat into work, i.e. when the reverse process occurs. The magnitude of this limit is established by the **reversible Carnot cycle** (1824). The latter consists of four consecutive reversible processes (Fig. 21): isothermal expansion AB during which the working body takes up heat Q_1 from the heat source (hot reservoir) having a temperature T_1; adiabatic expansion BC, isothermal compression CD during which the working body gives up a part of its heat Q_2 to a heat sink (cold reservoir) having a temperature T_2, and adiabatic compression DA. The processes of the removal and transfer of energy proceed at constant temperatures, since we can imagine that both heat reservoirs (the source and the sink) have such great dimensions (or with finite dimensions, such a great heat capacity) that the transfer of heat does not affect their temperature. As a result of the cyclic process, the system performs the work $W = Q_1 - Q_2$ numerically equal to the shaded area in Fig. 21. This cycle is called the direct (heat) Carnot cycle. In the reverse (refrigeration) Carnot cycle, the heat Q_2 is taken up from the heat sink and together with the external work W is transferred to the heat source, so that $Q_1 = Q_2 + W$ *.

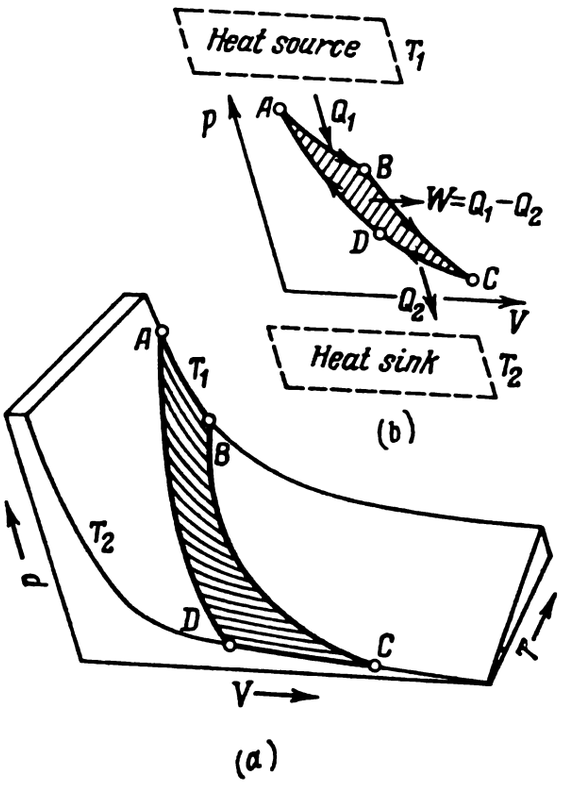


Fig. 21. The Carnot cycle (*a*) and a thermodynamic diagram of a heat engine (*b*)

The Carnot-Clausius Theorem. N. Carnot established that *the efficiency of a machine operating according to a reversible cycle does not depend on the nature of the working body, but on the interval of temperatures in which work is performed.*

Clausius confirmed the validity of this postulate by the following reasoning on two Carnot conjugate engines. Assume that when

* For a detailed analysis of the Carnot cycle see courses in engineering thermodynamics.

conducting a reversible Carnot cycle with two different bodies within the same temperature interval, we would get different efficiencies (η_1 and η_2). In this case, if the Carnot machine having the greater efficiency drove the one having the lower efficiency (i.e. the first cycle is conducted in the forward direction and the second in the reverse one), then energy would pass from the cold to the hot body without any compensation, i.e. a process would be conducted that contradicts Clausius's postulate. The truth of this statement can easily be seen, for example, by inspecting the following balance of the Carnot cycles:

	Q_1	Q_2	W	η
First cycle	+100	−80	+20	0.20
Second cycle	−110	+90	−20	0.18
Total	−10	+10	0	

It is not difficult to show that the case when $\eta_2 > \eta_1$ should also be excluded (in this case the first cycle should be conducted in the reverse direction, and the second in the forward one).

Thus, in accordance with the proved theorem, we have

$$\frac{Q_1}{Q_2} = \varphi(T_1, T_2) \text{ or } \eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = \varphi(T_1, T_2) \qquad (4.1)$$

To determine the function $\varphi(T_1, T_2)$ and to thus construct a temperature scale, we shall select the simplest form of relationship, assuming that the ratio of the heats equals that of the temperatures, i.e.

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad \text{or} \quad \eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \qquad (4.2)$$

The form of function (4.1) can also be determined in a different way. In accordance with the Carnot-Clausius theorem, it is sufficient to conduct a reversible Carnot cycle with any substance for which an equation of state is known. This makes it possible to express the processes forming the cycle through thermodynamic parameters of state, imparting a concrete expression to the right-hand side of Eq. (4.1). We shall assume that the working body is an ideal gas, since its properties are known from the molecular-kinetic theory. For an ideal gas, we have $pV = RT$, consequently (see Fig. 21)

$$Q_1 = \int_{V_A}^{V_B} p\,dV = \int_{V_A}^{V_B} RT_1 \frac{dV}{V} = RT_1 \ln \frac{V_B}{V_A}$$

$$Q_2 = \int_{V_D}^{V_C} p\,dV = RT_2 \ln \frac{V_C}{V_D}$$

Since BC and DA are adiabatic, in accordance with the equation of an adiabat of an ideal gas

$$T_1V_A^{\gamma-1} = T_2V_D^{\gamma-1} \quad \text{and} \quad T_1V_B^{\gamma-1} = T_2V_C^{\gamma-1}$$

(here $\gamma = C_p/C_V$), then

$$\frac{V_A}{V_D} = \frac{V_B}{V_C} \quad \text{or} \quad \frac{V_C}{V_D} = \frac{V_B}{V_A}$$

Inserting the results found into Eq. (4.1), we get Eq. (4.2).

The validity of the Carnot-Clausius theorem cannot be confirmed *only* by the fact that Eq. (4.2) does not include a characteristic of the substance (an ideal gas). In other words, we cannot omit the general proof of the theorem, because in passing over to a working body that differs from an ideal gas, it is impossible to see why we cannot find a reflection of any of its properties in Eq. (4.2).

It follows from Eq. (4.2) that the greater the temperature difference, the more completely is the heat of the heat source utilized. The reason for the comparatively low efficiency of a steam engine lies in the too insignificant interval between the boiling point and the temperature of condensation of water. Even in a modern steam engine using greatly superheated steam ($t_1 \approx 550\,°C$) and a special condenser ($t_2 \approx 10\,°C$), the efficiency according to Eq. (4.2) equals 0.65, while in practice it is considerably lower.

The efficiency can be improved by using other substances (for example mercury), but in practice steam is used almost exclusively owing to a number of advantages — its availability, great heat of vaporization, low unit weight, its relative inertness, etc. In internal-combustion engines, where ignition and the liberation of heat occur at very high temperatures, the efficiency is considerably higher.

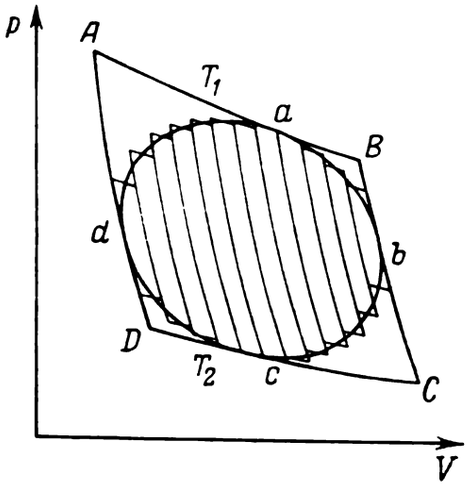


Fig. 22. Illustrating the proof of the Carnot theorem

The increase in the practical efficiency when going from one working body to another has nothing in common with the constancy in principle of the efficiency of a reversible Carnot cycle.

The Carnot Theorem. Any cycle can be replaced by an infinitely great number of infinitely small Carnot cycles each of which will differ from the corresponding elementary part of an arbitrary cycle by an infinitely small value of a higher order of magnitude (see Fig. 22). Consequently, the efficiency of arbitrary cycle *abcd* will be a certain average value of the efficiencies of elementary

Carnot cycles. But the efficiency of the Carnot cycle $ABCD$ within the same temperature interval will be greater than the efficiency of the cycle being considered, since, with a few possible exceptions, $T_1 > (T_1)_i$ and $T_2 < (T_2)_i$, where $(T_1)_i$ and $(T_2)_i$ are the temperatures on the elementary sections of heat exchange in cycle *abcd*. Hence, *no engine exists which would have an efficiency greater than that of a Carnot engine operating within the same temperature interval* (the **Carnot theorem**).

We can prove this theorem in a different way: in isothermal expansion (of an ideal gas), all the heat received from the heat source is converted into work, and the decrease in energy in adiabatic expansion also produces only work, i.e. both processes, if they are also reversible, are the most economical. Therefore, reverse compression along an isotherm and an adiabat is connected with the expenditure of the minimum work.

It follows from a reversible Carnot cycle having the maximum efficiency that this cycle establishes the limit of the conversion of heat into work at a given temperature difference.

The Carnot cycle thus occupies a special place among all other cycles and can be called the **basic thermodynamic cycle.**

4.1.2. Thermodynamic Temperature Scale

The fact that the efficiency of a Carnot engine does not depend on the nature of the working body made it possible to introduce a universal temperature scale free of the individual features (physical properties) of the thermometric substance and of the arbitrary nature of the method of measuring temperature. This scale was proposed in 1852 by W. Thomson (Kelvin) and was called the **absolute thermodynamic scale.**

The thermodynamic temperature scale is determined by Eq. (4.2), according to which the ratio between any two temperatures equals the ratio between the values of the heats received and given up by a heat machine reversibly functioning between these temperatures. The choice of the function $\varphi(T_1, T_2)$ [Eq. (4.1)] is arbitrary. It would have been possible to choose not T as this function, but T^{-1}, or e^T, or any other function of the absolute temperature.

A Carnot engine cannot be used to measure temperature as a special thermometer. Since the absolute temperature coincides, however, with the temperature entering the equation of state of an ideal gas, it can be measured with a thermometer filled with an ideal gas. This is one of the main conveniences of the choice of T as the function being considered.

The unit of temperature is taken equal to such a difference between the temperatures of a heat source and a heat sink which

makes it possible to perform one-hundredth of the work done by a body working according to a reversible Carnot cycle between the boiling point of water and the melting point of ice.

The second law of thermodynamics leads us to conclude that there exists a universal temperature, and thus there exists a temperature scale whose zero is the absolute zero of temperature (absolute zero). The value $T_2 = 0$ corresponds to the maximum (theoretical) value $\eta = 1$, according to Eq. (4.2), for any substance.

4.1.3. Impossibility of a Perpetual Motion Machine

Even in the most efficient machine, part of the heat cannot be converted into work. For further conversion to occur, a new machine is needed operating within the limits of the temperature of the heat sink and a higher temperature of the heat source.

Consequently, *it is impossible to construct an engine in which the working body would perform work as a result of heat exchange with a single source of heat,* for example to construct a periodically operating machine, all of whose operation would consist in performing work by cooling the heat source. In brief, *it is impossible to construct a perpetual motion machine of the second kind.*

This statement logically leads to the following: it is impossible to convert the heat of a body into work without performing any other change except for cooling this body; *it is impossible to perform work with the aid of a cyclic isothermal process.*

The impossibility of a perpetual motion machine of the first kind can be stated in two ways. On one hand, "work cannot be created from nothing"; on the other, "work cannot be converted into nothing". As regards the impossibility of a perpetual motion machine of the second kind, here inversion of the statement is excluded, since it is possible to construct a machine whose entire operation would consist in expending work and heating the heat source. This difference directly follows from the nature of heat: *chaotic* thermal motion of particles is more probable than their *directional* motion. The "appearance" of heat is always a sign that energy converts into a poorly effective form — the probability that chaotic motion would receive a definite orientation (this would result in the appearance of a directional force capable of performing work) is exceedingly negligible. This is the reason why the conversion of heat into work without any limitations is impossible, although work can be completely converted into heat.

Consequently, without the presence of a heat sink, the store of energy of a heat source cannot be utilized. It is impossible, for instance, to use the boundless stores of energy of the air, seas, oceans, the earth's crust, etc. If a perpetual motion machine of the

second kind were possible, then by converting the stores of heat in the water of the oceans into work, we could operate all the world's plants and factories, and only in about 1000 years would the temperature of the water drop by about 0.01 K.*

Example 1. Prove, on the basis of the impossibility of the complete (uncompensated) conversion of heat into work, that the processes of friction and expansion of a gas in a vacuum are irreversible.

Solution. In friction, the work to overcome the forces of friction is spent for heating. Since the reverse process, i.e. the uncompensated conversion of Q into W, is impossible, the process of friction is also irreversible.

The diffusion of a gas into a vacuum is also irreversible, since a process whose only result would be the compression of a gas without changing its energy is impossible. Indeed, a certain amount of work W is spent for compression, and to ensure that $\Delta U = 0$, it is necessary to simultaneously remove the heat Q. But for no traces of the given process to remain in the surroundings, it would be necessary to convert Q into W without any compensation, which is impossible.

Example 2. Prove that

(1) an adiabat can intersect an isotherm only at one point;

(2) when a process proceeds along an adiabat, the temperature always changes in one direction.

Solution. 1. If the two curves intersected at two points, we would get a cycle formed by one isotherm and one adiabat. In this case, work would be performed with only one existing source of heat, which contradicts the second law.

2. If the temperature did not change in one direction, the same temperature could be encountered at two points of the same adiabat, which on the basis of the preceding material is impossible.

Example 3. When conducting a Carnot cycle in the reverse direction (a refrigeration cycle), heat is transferred from the refrigerator to the heater by the work done. The efficiency of such a cycle (the refrigerating factor) determines the amount of heat removed from the refrigerator per unit of work done. In 1853, Kelvin proposed to use this cycle for heating dwellings by taking away heat from the cold air. Show the effectiveness of such "heating". Assume that

(1) the interval of temperatures in which a steam engine operates is 180-40 °C and $\eta = 0.66\eta_{\text{theor}}$;

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* A perpetual motion machine using the energy of the ocean water should not be confused with an engine operating by the *difference* in temperatures at the surface and in the depth of an ocean.

(2) the temperature of the air indoors is 20 °C, and outdoors is 10 °C;

(3) the steam engine and the refrigerating machine operate according to a reversible Carnot cycle.

Solution. The steam engine driving the refrigerating machine operates with the efficiency

$$\eta_{\text{theor}} = \frac{180 - 40}{180 + 273.2} = 0.309$$

Consequently, about one-third of the heat brought into the engine by the steam is converted into work, i.e. $\eta \approx 0.66 \times 0.309 \approx 0.204$, or 20.4% of the heat developed by the fuel.

The refrigerating factor of the refrigerating machine is $(10 + 273.2)/(20 - 10) = 28.3$. Consequently, by expending mechanical work equivalent to one calorie, we can transfer 28.3 cal from the cold to the hot body. The steam engine converts $0.204Q$ cal into work. Expending this work in the refrigerating machine, we transfer from the air outdoors into the premises $28.3 \times 0.204Q = 5.77Q$ cal of heat instead of the Q cal which would be at our disposal upon the direct combustion of the fuel.

Thus, theoretically this method is even more advantageous than the direct combustion of the fuel, which would give us a maximum of Q cal, let alone conventional heating when an enormous amount of heat is carried away into the chimney.

The above principle served as the basis of "dynamic heating" developed in 1926 by Prof. V. Mikhelson of the Timiryazev Agricultural Academy in Moscow.

Example 4. Figure 23 shows a theoretical isotherm *AaBcbD* of a real gas. How can the position of straight line *ab* corresponding to the saturated vapour pressure at a given temperature be determined without resorting to an experiment?

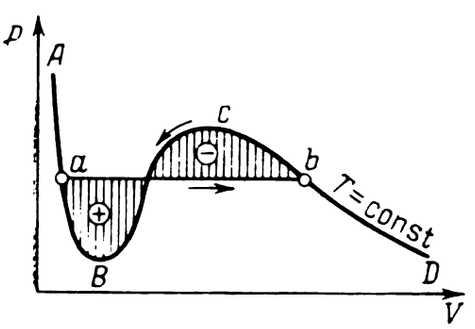

Fig. 23. Isotherm of a real gas (the shaded areas are equal).
(See Example 4)

Solution. In a cyclic process along the contour *abcBa* (a reverse isothermal cycle), we have $\oint p\,dV = 0$. Therefore, the isobar should be drawn in such a way that the shaded areas in Fig. 23 are equal.

4.2. ENTROPY

The first law is defined by the constancy of the function U in an isolated system. Let us find a function expressing the essence of the second law, namely, the *single direction* of the processes in

an isolated system. The change in the function being sought should have the same sign for all real, i.e. irreversible, processes in isolated systems. Thus, unlike the first, the second law as applied to non-cyclic irreversible processes should be expressed by an *inequality*.

4.2.1. Change in Entropy in Reversible Processes

Again considering the heat received from a heat source to be positive and that given up to a heat sink negative, we can write down Eq. (4.2) in the form

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \quad \text{or} \quad \sum \frac{Q}{T} = 0 \tag{4.3}$$

If we break up Q_1 and Q_2 into infinitely small quantities, then Eq. (4.3) becomes

$$\int \frac{\delta Q_1}{T_1} + \int \frac{\delta Q_2}{T_2} = 0 \tag{4.4}$$

Since any cycle can be replaced by an infinitely great number of infinitely small Carnot cycles (see Fig. 22), then Eq. (4.4) holds for any reversible cycle. The only difference is that owing to the non-isothermal nature of the processes of heat exchange, the conducting of an arbitrary reversible cycle will require an infinitely great number of heat sources (on path *dab*) and heat sinks (on path *bcd*).

Considering that $T = \text{const}$ on each elementary section of heat exchange, we find that

$$\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0$$

and for the entire cycle

$$\int_{1\,(dab)}^{2} \frac{\delta Q_1}{T_1} + \int_{2\,(bcd)}^{1} \frac{\delta Q_2}{T_2} = 0 \quad \text{or} \quad \oint \frac{\delta Q}{T} = 0 \tag{4.5}$$

Consequently, *the algebraic sum of the reduced heats* $\delta Q/T$ *for any reversible cyclic process equals zero.*

It follows from Eq. (4.5) in accordance with Eq. (1.7) that the integrand is a full differential, i.e. a differential of an unambiguous function of state. This new function was introduced into thermodynamics by Clausius (1865) and called entropy (from the Greek "tropē" — "transformation"). Its symbol is S. Since on the basis of the Carnot-Clausius and Carnot theorems, the above reasoning can be applied to any substance and to any cycle, then a system

in any state has a quite definite and single value of entropy, just like it has a definite and single value of p, V, T, U and other properties.

Entropy is thus expressed by the equation

$$dS \equiv \frac{\delta Q}{T} \tag{4.6}$$

This is a function of state of a system defined by the fact that its differential in an elementary equilibrium process is equal to the ratio between the infinitely small amount of heat communicated to a system and the thermodynamic temperature of the system.*

It is significant that the *absolute* temperature figures in Eqs. (4.5) and (4.6), whereas in the equations given earlier t may be substituted for T. In other words, entropy is related to the absolute, and not to the empirical, temperature. *The quantity* $1/T$ *is an integrating factor, and the absolute temperature an integrating divisor for* δQ.

N. Shiller (1896) proved the existence of a single integrating factor common for all bodies. His ideas were developed in the work of C. Carathéodory (1909). K. Putilov (1937) developed another way of substantiating entropy and absolute temperature (see [A49]).

For a finite change in a system **

$$\Delta S = \int_1^2 \frac{\delta Q}{T} \tag{4.7}$$

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* It should be noted that according to Carnot, who proceeded from the theory of thermogen in constructing the theory of heat engines, Eq. (4.5) should be written down as $\oint \delta Q = 0$. Hence it would be possible to conclude that thermogen is an analogue of entropy; according to the thermogen theory, if a body contains a different store of heat in the initial than in the final state, then no matter how a process takes place, an identical amount of heat must be supplied (or withdrawn). Although this is not correct, the same could be said with regard to reversible processes about the sum of the heats that was said relative to the sum of the reduced heats.

** If the dependence of work on the nature of a process could be confirmed, for example Fig. 3 (p. 31) on condition that $y = p$ and $x = V$, then by introducing the function S, the dependence of heat on the nature of a process can be graphically illustrated. Indeed, if $y = T$ and $x = S$, then by Eq. (4.6) the quantity

$$Q = \int_1^2 T\, dS$$

will be proportional to the area under the curve of the process (in the coordinates T-S).

For an isothermal process, Eq. (4.7) becomes

$$\Delta S = \frac{Q}{T} \tag{4.8}$$

and for an adiabatic one it becomes

$$\Delta S = 0, \; dS = 0 \tag{4.9}$$

It is premature to state that entropy is the needed function, since the relationship between its change and the direction of a process is not yet clear.

4.2.2. Change in Entropy in Irreversible Processes

Let us write down Eq. (2.3) for a reversible and an irreversible processes with the initial and final states coinciding. Since the change in energy in both cases is the same, while the work in an irreversible process is less than in a reversible one (see Sec. 1.2.4), then the heat absorbed by a system in an irreversible process will be less than in a reversible one (the liberated heat, on the contrary, will be greater). But since the change in the entropy of the system in both processes is the same, then Eqs. (4.5-4.9) respectively become

$$\oint \frac{\delta Q}{T} < 0 \tag{4.10}$$

$$dS > \frac{\delta Q}{T} \tag{4.11}$$

$$\Delta S > \int_1^2 \frac{\delta Q}{T} \tag{4.12}$$

$$\Delta S > \frac{Q}{T} \tag{4.13}$$

$$\Delta S > 0, \quad dS > 0 \tag{4.14}$$

Thus, *equations* (4.5) to (4.9), which are analytic expressions of the second law for various *reversible* processes, turn into *inequalities* (4.10) to (4.14) upon passing over to *irreversible* processes.

In exactly the same way, because of the condition $W_{\text{irrev}} < W_{\text{rev}}$, for irreversible cyclic processes Eq. (4.2) transforms into the inequality

$$\frac{Q_1 - Q_2}{Q_1} < \frac{T_1 - T_2}{T_1}$$

In contrast to Eq. (4.2), T_1 and T_2 do not equal the temperatures of the working body on the corresponding sections of heat exchange.

4.2.3. Change in Entropy as a Criterion of the Equilibrium and Spontaneity of Processes

Let us generalize expressions (4.9) and (4.14) for any process. To do this, a system must be isolated, i.e. a heat source (or sources) included in it. But in this case the change in the entropy of the system will be formed from the change in the entropy of the "working" part of the system (where the process takes place) and the change in the entropy of the heat source. Thus, we get

$$\Delta S = (\Delta S_{\text{work.syst}} + \Delta S_{\text{heat source}}) \geqslant 0 \qquad (4.15)$$

i.e. *if a system is isolated, then its entropy does not change when reversible processes occur in it, and its entropy grows when irreversible processes take place.* When an irreversible process brings an isolated system to a state of equilibrium, its entropy reaches a *maximum.* Consequently, the entropy is a criterion of the *direction* of a process ($\Delta S > 0$), and, therefore, a criterion of equilibrium ($\Delta S = 0$).

The division of all processes into ones spontaneous and unspontaneous under the given conditions has thus found its quantitative expression. Since the inequality $\Delta S < 0$ is a criterion showing that processes are impossible, *a process cannot take place in an isolated system if it is connected with a decrease in entropy.*

It should again be stressed that the condition $\Delta S \geqslant 0$ covering all possible cases relates only to an *isolated* system as a whole. Processes may take place in separate parts of the system for which $\Delta S < 0$. In other words, in a non-isolated system, both irreversible and reversible processes can also occur with a decrease in entropy.

In this connection, it is necessary to distinguish between calculations to determine the *value* of ΔS in a process and calculations to determine the *feasibility* of a process. In the first case, we must find ΔS for only a part of a system, whereas in the second case, we always have ΔS for an *isolated* system (which is a working system only in the absence of heat exchange).

Thus, the problem of finding a function expressing the unidirectional nature of the processes in a system has been solved. The irreversibility of processes is measured by the entropy. The constancy of the entropy in reversible processes only confirms the fact that this function characterizes the lack of uniformity in the states of a system at any moment of an irreversible process: at any two moments of a reversible process in an isolated system its states from

the standpoint of the possibility of further changes are equivalent to each other, since the "workability" of the system does not change.

This circumstance can be confirmed by the following example.

The transfer of heat from a hot to a cold body is irreversible. For this reason, the "growth in the amount of heat" in a system is more irreversible at a low temperature than at a high temperature. Indeed, using a system where the second process occurs as a heat source, and the system where the change occurs at a lower temperature as a heat sink (provided that both systems are isolated from the surroundings), we can perform a Carnot cycle between them and obtain a certain amount of work. At the same time, other conditions being equal, a process is the more irreversible, the greater is the amount of heat transferred, since not only does heat pass from a higher level to a lower one, but also all kinds of energy in any process tend to transform into heat, which is also irreversible. If this reasoning is compared with the expressions determining ΔS, then the statement that entropy is a measure of the irreversibility of a process will become obvious.

For a reversible process, the equations relating S, Q and T will contain T_{max}, because when other conditions are equal, the efficiency is the greater, the higher is the temperature of the heat source. This can be noted by rewriting Eq. (4.2) in the form $\eta = 1 - T_2/T_1$. For an irreversible process, the temperature will be minimum. The greater the irreversibility of a given process (at identical values of T_1 and T_2), the higher is the value of Q_2 [Eq. (4.2) transforms into an inequality], and, consequently, the higher is the value of ΔS. The unused heat can be utilized by diminishing T_2, but this involves the expenditure of work.

It would seem that the use of entropy for solving *practical* problems is not justified, since *inequality* signs figure in all the expressions relating to irreversible processes, for instance in expression (4.13), and it is therefore impossible to calculate ΔS even if we do know the characteristics of an irreversible process. It is quite simple to circumvent this difficulty, however. To calculate ΔS, it is sufficient to assume that the given process is reversible, in other words, it should be mentally replaced with such a combination of reversible processes so that the system reaches the same final state that it actually does. Indeed, such a procedure makes it possible to calculate ΔS, because the expressions used in the calculations of reversible processes are *equations*. At the same time, the value of ΔS found in this hypothetical way is the change in the entropy in the actual process, since this change does not depend on the nature of the transformation. (This is why the impossibility of conducting

a reversible process cannot hinder the application of the procedure described above.)

It is now clear why we introduced the function S for reversible processes and only then extended it to irreversible ones.

In conclusion, we shall consider a way of substantiating the *existence* of the function S without involving the Carnot cycle. In a reversible process, the pressure equals the counterpressure, and we can insert its value from the equation of state $\varphi(p, V, T) = 0$ instead of the external pressure in Eq. (2.5). Therefore, for a reversible process Eq. (2.5) becomes

$$\delta Q = dU + \varphi(V, T)\, dV$$

whence

$$\int_1^2 \delta Q = \int_1^2 dU + \int_1^2 \varphi(V, T)\, dV$$

The quantity $\int_1^2 dU$ is fixed at given initial and final states of a system. A new value of T (which will depend on the nature of the process), however, will correspond each time to each value of V. Consequently, it is impossible to integrate the second term of the right-hand side of the equation, and also δQ (the latter is not a full differential). Naturally, if we consider an isothermal process, then integration will become possible, one variable remaining in the integrand. But this is not a general solution, since a restriction is imposed.

Hence, to transform the equation of the first law of thermodynamics for a reversible process into an integrable expression, an integrating factor must be introduced. We shall determine the integrating factor in a very simple *particular* case for an ideal gas, because its properties (the relationship between p, V and T and the dependence of U on other parameters)

$$p = \varphi(V, T) = \frac{RT}{V} \quad \text{and} \quad dU = \left(\frac{\partial U}{\partial T}\right)_V dT = C_V\, dT$$

can be found from the molecular-kinetic theory (owing to the absence of forces of interaction, the internal energy of an ideal gas depends only on temperature). In this case, Eq. (2.5) becomes

$$\delta Q = C_V\, dT + RT\, d \ln V$$

Dividing this equation by T gives us an expression that can be integrated. Indeed, the coefficients of the variables in the expression

$$\frac{\delta Q}{T} = C_V d \ln T + R d \ln V$$

comply with Eq. (1.5), since

$$\frac{\partial C_V}{\partial \ln V} = \frac{\partial R}{\partial \ln T} = 0$$

Thus, the quantity $\delta Q/T$ is a full differential. Hence, relationship (4.6) holds, and, consequently, the *existence* of the function S for an *ideal* gas has been proved.

To generalize expression (4.6) for any substance, we can turn to the Carnot-Clausius and Carnot theorems, i.e. repeat our previous reasoning, or, which is simpler, reason as follows.

If an isolated system in which an elementary reversible process occurs consists of an ideal gas and any other substance, then $\delta Q = \delta Q_{\text{id.gas}} + \delta Q_{\text{subst}} = 0$. Since $dS_{\text{id.gas}} = \delta Q_{\text{id.gas}}/T$, then $T\,dS_{\text{id.gas}} + \delta Q_{\text{subst}} = 0$ and $dS_{\text{id.gas}} = -\delta Q_{\text{subst}}/T$.

Therefore, the quantity $\delta Q_{\text{subst}}/T$ is also a full differential, i.e.

$$dS_{\text{subst}} = \frac{\delta Q_{\text{subst}}}{T}$$

Thus the *existence* of the function S has been proved for any substance.

Does this mean that the second law is a corollary of the first? Clearly not, since the above course of the proofs requires the concept of the reversibility and irreversibility of processes to be introduced. A proof of the *growth* of the entropy in irreversible processes in an isolated system (and it is exactly this circumstance that reflects the essence of the second law) can be given, however, only by reasoning which does not follow from the first law.

While the method of introducing the function S set out above has the advantage of simplicity and clarity, the one set out on pp. 88-91 and 94-97 makes it possible to introduce the function S without resorting to the properties of a concrete substance in the reasoning. This justifies the use of the general equations for finding the properties of an ideal gas derived on following pages (see Sec. 6.1).

Example 5. Can an equality sign be placed between an adiabatic and an isentropic processes?

Solution. No, because both terms correspond to the same process only when it is reversible [cf. expressions (4.6) and (4.11)].

Example 6. By the quantity T in the expressions showing the change in the entropy in irreversible processes is usually meant not the temperature of the system, but that of the heat source. What is the reason for the convenience of such a substitution? Can it not lead to "equalization" of the corresponding inequalities, for example of inequality (4.13)?

Solution. The convenience of such a substitution is that with irreversible heat exchange the value of the temperature of the system becomes indefinite. At the same time, this substitution cannot lead to distortions, since the inequalities used to express ΔS of the system in irreversible processes become greater when $T_{\text{heat source}}$ is substituted for $T_{\text{work. syst}}$. Indeed, when a system receives heat, the temperature in the denominator of the right-hand side of the inequalities will be greater; when heat is given up, although the temperature of the heat source is greater than that of the working system, the right-hand side of the inequality again diminishes algebraically because Q is less than zero.

Example 7. Show that when two pieces of metal are brought into contact, the process of levelling out of their temperatures is irreversible.

Solution. We form a closed system from the contacting metals A and B, for which purpose we enclose them in an adiabatic envelope. Since the temperature constantly changes in the course of heat exchange, we shall divide the process into a number of elementary ones. If each of them were reversible, then the sum

$$dS = -\frac{\delta Q}{T_A} + \frac{\delta Q}{T_B}$$

would equal zero (we assume that the temperature remains constant in each elementary process). Actually, since $T_A > T_B$, then $dS > 0$. Summation for the entire process yields $\Delta S > 0$. Consequently, the process is irreversible.

4.2.4. Relation Between Entropy and Other Thermodynamic Parameters and Some Relationships Between Derived Functions

To solve specific problems connected with the use of entropy, we must establish the relationship between it and other thermodynamic parameters.

Let us limit ourselves to a few equations.

Equation (4.6) in combination with Eqs. (2.5) and (2.12) gives

$$dU = T\,dS - p\,dV \tag{4.16}$$

$$dH = T\,dS + V\,dp \tag{4.17}$$

which may serve as a mathematical formulation combining both laws of thermodynamics. Like Eqs. (2.5) and (2.12), they hold for any substance, but, in contrast to the latter, only for reversible processes.

Writing down Eq. (1.8) in conformity with the functional relationship $\varphi(T, V, S) = 0$, we get

$$\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_V = -1$$

Combining the latter with the equation

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

obtained from Eq. (4.16) on the basis of Eq. (1.5), we find after transformation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{4.18}$$

Similarly, from Eq. (1.8), written down for the relationship $\varphi(T, p, S) = 0$, and from Eq. (1.5) as applied to (4.17), we get

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \tag{4.19}$$

Finally, from Eqs. (3.9), (3.10) and (4.6), we find the temperature dependence of the entropy for an isochoric process

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \tag{4.20}$$

and for an isobaric one

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \tag{4.21}$$

The last two equations are practically the most important particular cases of the general relationship (see also Sec. 7.4)

$$T\,dS = C\,dT \tag{4.22}$$

Using these relationships, we can derive a number of general equations relating various thermodynamic parameters.

In conclusion, we shall give two more equations:

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V \tag{4.23}$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p \tag{4.24}$$

The first is obtained by differentiating Eq. (4.17) and then using Eq. (4.19); the second by differentiating Eq. (4.21) and then using the same equation.

Example 8. Find ΔS for the process of crystallization of benzene at (1) $t = 5$, and (2) $t = -5\,°C$ if $(\Delta H_m)_{278} = 2370$ cal/mol, C_p for liquid benzene is 30.3 and for crystalline benzene 29.3 cal/mol·K.

Solution. 1. Since the process is reversible, we use Eq. (4.8) to find ΔS for benzene:

$$\Delta S = S^c_{278} - S^{lq}_{278} = -\frac{\Delta H_m}{T_m} = -\frac{2370}{278.2} = -8.52 \text{ e.u. (entropy units)}$$

(1 e.u. = 1 cal/mol·K), i.e. the entropy of crystalline benzene is less than that of liquid benzene by 8.52 e.u. It is not correct to state that the given process is impossible on the grounds that here $\Delta S < 0$, because the system is *not an isolated one.*

If the system is isolated and a heat source is included in it, then $\Delta S = \Delta S_{\text{benzene}} + \Delta S_{\text{heat source}} = -8.52 + (2370/278.2) = 0$, which is what should be expected, because the process is reversible.

2. Since there is no thermodynamic equilibrium between supercooled liquid benzene and crystalline benzene, the second process is irreversible, i.e. in this case Eq. (4.8) may not be used for the calculations — in the given case $\Delta S > (-2360/268.2)$ *. To calculate ΔS, we must mentally conduct the process reversibly, i.e. infinitely slowly (at p = const), and in such a way that at each moment the temperature of the working body (benzene) would coincide with that of the heat source, or, more precisely, would differ from it by an infinitely small amount. First we conduct reversible heating of the liquid benzene from −5 to +5 °C. For this purpose, we bring it into contact with a heat source or into consecutive contact with a very great number of heat sources on the condition that the temperature of each successive source is higher than that of the preceding one by an infinitely small value. Next we crystallize the benzene (this process is reversible at $t = +5\,°C$) and, finally, reversibly cool the crystalline benzene formed to $t = -5\,°C$. The total change in the entropy in all three stages will obviously give the desired quantity.

* It is simple to assess the numerator with the aid of Eq. (3.38).

What has been set out above can be represented diagrammatically:

$$\begin{array}{ccc} C_6H_6(lq,\ t=-5) & \xrightarrow{\Delta S=?} & C_6H_6(c,\ t=-5) \\ \downarrow \Delta S_1 & & \uparrow \Delta S_3 \\ C_6H_6(lq,\ t=+5) & \xrightarrow{\Delta S_2} & C_6H_6(c,\ t=+5) \end{array}$$

On the basis of Eq. (4.21) and the data given in the initial conditions of the present example, we have

$$\Delta S_1 = \int_{268.2}^{278.2} 30.3 \frac{dT}{T} = 1.11 \text{ e.u.}$$

$\Delta S_2 = -8.52$ e.u. (see the solution of the preceding problem)

$$\Delta S_3 = \int_{278.2}^{268.2} 29.3 \frac{dT}{T} = -1.07 \text{ e.u.}$$

Therefore, $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -8.48$ e.u.

To draw a conclusion about the possibility of this process, we must isolate the system, hence, $\Delta S = -8.48 + (2360/268.2) = 0.31$ e.u., i.e. $\Delta S > 0$, which should be expected, since this process is irreversible.

Example 9. Find the change in the entropy for the process $Ag + \frac{1}{2} Cl_2(g) = AgCl$ if $p = 1$ atm and $t = 25\,^\circ C$.

Solution. From Table 1, we find $\Delta H^\circ_{298} = -30\,730$ cal/mol. Since the given process is irreversible, we have $\Delta S > (-30\,730/298.2)$ e.u. If this reaction is conducted in a galvanic cell placed in a thermostat and a constant temperature and pressure are maintained in the cell, and if the e.m.f. of the cell is *compensated* by an e.m.f. applied from outside, then the process will be practically reversible. The work done will be $W'_{max} = zEF$ (z is the number of gramme-equivalents and F the Faraday constant), while the heat effect Q in accordance with Eq. (4.8) will equal $T\Delta S$. It is obvious that

$$\Delta U = Q - W_{max} = Q - (p\,\Delta V + W'_{max})$$

or

$$Q = \Delta H + W'_{max} = \Delta H + zEF$$

Introducing into the latter equation the values of ΔH_{298} (the change in enthalpy does not depend on the course of the process, therefore it will be the same in both an irreversible and a reversible processes), $z = 1$, $E_{298} = 1.1362$ V and $F = 23\,062$ (the Faraday constant

reduced to calories), we get $Q = 30\,730 + 1 \times 1.1362 \times 23\,062 = -4526$ cal/mol.

Therefore, $\Delta S = -4526/298.2 = -15.18$ e.u.

The change in the entropy of the isolated system as a whole (i.e. the reacting system plus the thermostat) in the actual process will be $\Delta S = -15.18 + 30\,720/298.2 = 87.84$ e.u., which confirms the irreversibility of the process.

Note. See also Examples 5 and 7 in Chap. 6 (pp. 147, 148).

4.3. SUBSTANTIATION OF THE SECOND LAW

4.3.1. Thermodynamic Probability of a State

The same **macrostate** of a system, i.e. a state determined by the thermodynamic parameters, may exist (provided that the mean energy is constant) with a varying distribution of the energy between separate molecules; in other words, there is a very great number of **microstates.**

The number of microstates by which a given macrostate can be created is called the thermodynamic probability. In contrast to the mathematical probability, which in accordance with its definition (the ratio of the number of cases favouring a given occurrence to the total number of *equally possible cases*) varies within the limits from zero to unity, the thermodynamic probability is always greater than unity and usually has a very large value. The mathematical probability of a state is obviously equal to the ratio of the thermodynamic probability of the state to the total number of possible microstates having the same energy.

We shall consider all microstates to be *equally probable.* This means that when a system subordinated to definite constant macroscopic conditions (temperature, pressure, etc.) is considered for a sufficiently long time, the probability of finding it in a definite microstate is identical for all possible microstates. In other words, in the course of time a system must pass through all the microstates corresponding to a given macrostate.

4.3.2. Phase Space

The state of every molecule is determined by three constituent positions (the three axes of space coordinates x, y and z) and three components of motion (three axes for reading off the velocity of motion or the momentum, i.e. the product of the mass and the velocity vector components mv_x, mv_y and mv_z). It may thus be depicted in a six-dimensional "space" which is called a **gamma-** or **phase space.** This is a space of coordinates and momenta whose complex exhaustively characterizes the state of a system at any

moment (in contrast to real space it may have any number of dimensions).

Let us divide a phase space into a number of cells each having the edges dx, dy, dz, $d(mv_x)$, $d(mv_y)$ and $d(mv_z)$. The "volume" of a cell equals $dx \cdot dy \cdot dz \cdot d(mv_x) \cdot d(mv_y) \cdot d(mv_z)$. A given phase cell contains molecules whose coordinates are confined within the limits from x to $x + dx$, from y to $y + dy$, etc. It now becomes possible to distribute all the molecules of a system according to the values of their coordinates between the corresponding cells of the phase space, and the distribution of the molecules permits us to find the number of microstates corresponding to a given macrostate, i.e. the thermodynamic probability.

In other words, it is considered that the nature of distribution of the molecules within a given phase cell does not create a new microstate.

Thus, to find the thermodynamic probability of a state, one must count the number of combinations by means of which a given spatial distribution can be carried out. This quantity is determined by the number of permutations of the number of particles present taken all at a time. If the given system contains N molecules, then the total number of permutations will be $N!$. It is necessary to exclude from this number the permutations that do not give new microstates, i.e. which consist in permutation of the molecules within each phase cell. The number of such permutations will be $N_i!$, where N_i is the number of molecules in the i-th cell. It can be proved that the thermodynamic probability

$$P = \frac{N!}{N_1!N_2!N_3!\ldots} \tag{4.25}$$

where

$$N = N_1 + N_2 + N_3 + \ldots$$

To obtain a new macrostate, it is necessary to change the spatial distribution, i.e. to change the nature of distribution of the molecules in the phase space.

Example 10. Find the thermodynamic probability for a system consisting of 10 molecules. Their phase distribution is hypothetically shown in Fig. 24 where each square corresponds to a phase cell, and each circle to a molecule.

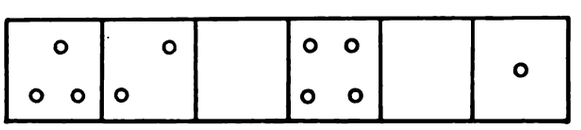

Fig. 24. A schematic illustration of phase distribution.
(See Example 10)

Solution. By Eq. (4.25)

$$P = \frac{10!}{3!2!4!1!} = 12\,600$$

Therefore, the given macrostate corresponds to 12 600 different microstates, i.e. this ten-molecule system may be created in 12 600 ways. Even such an insignificant increase in the "order" as, for example, the transition of one of the molecules from the fourth to the fifth phase cell leads to a four-fold increase in the thermodynamic probability.

4.3.3. Relationship Between Entropy and Thermodynamic Probability

What has been said above allows us to establish a relationship between entropy and thermodynamic probability. On one hand, the processes in an isolated system are attended by a growth in entropy, and, on the other, all natural processes consist in the transition of a system from a less probable to a more probable state, i.e. in a gradual transition to the state of equilibrium and, therefore, to an equalization of the "levels" of the microstates. This corresponds to a growth of the thermodynamic probability. The value of P in accordance with Eq. (4.25) can be increased only by decreasing the denominator of the equation (since the system is isolated, then $N = \text{const}$). Upon more and more uniform distribution of the molecules among the cells of the phase space, the denominator will diminish, and in the limit, when $N_1 = N_2 = N_3 = \ldots$, it will acquire the minimum value. The entire fraction and, consequently, the thermodynamic probability, will accordingly become maximum. The maximum value of the thermodynamic probability shows that a state of equilibrium has set in. Hence, the higher the value of P, the easier it is to realize a given state.

For a reversible process, the probability of the initial state coincides with that of the final and of any intermediate state, since all these states are equilibrium ones and correspond to the same (maximum) probability. This is the reason why reversible processes are not attended by a change in entropy. But this conclusion holds only for adiabatic or isolated systems. If a process (even a reversible one) is connected with heat exchange, then the entropy changes, because the reception or removal of heat introduces "disorder"; thus the possibility is created of determining ΔS by Q.

What is the nature of the dependence of entropy on thermodynamic probability? Being an extensive property, the entropy for

independent systems is additive.* This means that the entropy S of a system composed of two independent systems having the entropies S_1 and S_2 equals

$$S = S_1 + S_2$$

or

$$\varphi(P_{1+2}) = \varphi(P_1) + \varphi(P_2)$$

where P_{1+2} is the probability that system 1 has the entropy S_1 and that system 2 simultaneously has the entropy S_2.

The probability that a set of independent events will happen equals the product of their separate probabilities.** Hence, for independent systems we have

$$P_{1+2} = P_1 P_2$$

But since $S = \varphi(P)$, then from a comparison of the last two equations it follows that $S = \text{const ln } P$.*** The proportionality factor in this equation equals the Boltzmann constant $k = R/N_A$ [here N_A is the Avogadro constant (see Chap. 6, Example 6)]. Therefore

$$S = k \ln P \tag{4.26}$$

---

* The entropy of a solution or a chemical compound differs from the sum of the entropies of its constituent parts (by the change in the entropy in the *process* of solution or chemical interaction, respectively).

** We can illustrate this theorem by the following simple example. The probability of *simultaneously* extracting two red balls from two bags each containing nine white and one red balls is $\frac{1}{100}$, i.e. the product of the probabilities of extracting a red ball from each bag $\left(\frac{1}{10} \times \frac{1}{10}\right)$, on the condition that the extraction of any ball is *equally probable*.

*** The correctness of this relationship can be confirmed as follows. Since $P_{1+2} = P_1 P_2$, then

$$\varphi(P_1) + \varphi(P_2) = \varphi(P_1 P_2)$$

We take partial derivatives of the last expression with respect to P_1 and P_2. We get, accordingly,

$$\varphi'(P_1) = \varphi'(P_1 P_2) P_2 \quad \text{and} \quad \varphi'(P_2) = \varphi'(P_1 P_2) P_1$$

Division of the first of these equations by the second yields

$$\frac{\varphi'(P_1)}{\varphi'(P_2)} = \frac{P_2}{P_1} \quad \text{or} \quad \varphi'(P_1) P_1 = \varphi'(P_2) P_2$$

or, finally, in the general form

$$P\varphi'(P) = \text{const}$$

Integration of the last equation gives

$$\varphi(P) = \text{const ln } P$$

This is the **Boltzmann equation** (1887). We shall return to it in Sec. 13.7.1.*

The concept of entropy, which students find difficult to understand in the light of the conventional interpretation of the second law of thermodynamics, becomes clearer if explained statistically; it is precisely in its statistical interpretations that the true meaning of the second law is disclosed. The expediency of applying the statistical method is quite obvious, since entropy is related to heat and temperature, which owe their existence to the corpuscular structure of matter. A statistical substantiation of the second law was given in the works of L. Boltzmann, N. Pirogov, M. Smoluchowski, etc.

The statistical nature of the second law permits us to conclude that an increase in entropy reflects only the *most probable* paths of development of processes. No matter how low the probability of a process is, it must occur some time or other if the phenomenon is observed for a sufficiently long period. In other words, a decrease in entropy is not impossible, but only slightly probable. Thus irreversibility, and, consequently, the statement that the spontaneous diminishing of the entropy in adiabatically isolated systems is impossible, are deprived of their absolute meaning, and the second law of thermodynamics appears as a *law of probability*. This is its difference from the first law, which is *absolute*.

4.3.4. Fluctuations

When the number of particles is great, deviations of their number (in a unit of volume) from the mean value always occur that cause slight changes in the properties of a system to either direction of the mean values. Owing to the chaotic motion of the particles, this difference in the number of molecules in equal parts of the total volume of a system constantly changes. For this reason, all statistical quantities such as density, the concentration of solutions, pressure and temperature are subjected to spontaneously occurring *random* deviations from a certain mean value generally used for calculations. These deviations are called **fluctuations.** They explain such phenomena as the colour of the sky, in part the blue colour of the oceans, and opalescence at the critical point.

The practical significance of fluctuations is exceedingly great. They are the cause of the *gradual* nature of changes. Such processes

* Knowing the absolute values of the entropies (see Chap. 13), we can also assess the scale of the values of P for systems of a usual size. Thus, for hydrogen in accordance with Eq. (4.26) and Table 20, we get

$$\log P = \frac{31.195 \times 6.023 \times 10^{23}}{1.987 \times 2.303} \approx 10^{25}, \text{ i.e. } P \approx 10^{10^{25}}$$

as crystallization, the formation of a fog and many others would occur without them in a completely different manner.

It is quite natural that fluctuations are particularly important for systems having a negligible size. Thus, according to Smoluchowski's calculations, if the time needed for the *spontaneous* compaction of air by 1% for a volume having a radius of 1 cm is $10^{10^{14}}$ s, then for a radius of 10^{-5} cm it is only one second.

Fluctuations make it impossible to measure a quantity with a very high degree of accuracy. For instance, to detect a current in a circuit, its intensity must be greater than the fluctuation of the intensity. At present, only electrical instruments have reached such a high degree of accuracy that the fluctuations affect their functioning (the "creeping of zero" in a galvanometer, the shot effect in a photocell, etc.).

A classical example of the formation of fluctuations, i.e. of the appearance in equilibrium systems of processes occurring with a decrease in entropy, is **Brownian movement.** It appears because the sum of the impulses due to impacts of molecules of the medium against the surface of a tiny particle does not equal zero, and at each moment chaotically changes both in magnitude and in sign. This causes the particles to move upward notwithstanding the force of gravity and contrary to the second law (in its non-statistical formulations), since Brownian movement occurs in a medium where thermal equilibrium has already set in. Such contradictions between facts and theory disappear upon a statistical interpretation of the second law of thermodynamics.

Since in real systems the number of particles is very great, the fluctuations themselves and the deviations from the course of a process corresponding to thermodynamic laws caused by them will be negligibly small. Therefore, the most probable direction of a process in ordinary systems coincides with its actual direction. In other words, an event acquires the nature of inevitability. Consequently, the reason for the irreversibility of processes is the very great number of particles in ordinary systems. Phenomena occurring on the boundary between macro- and microsystems (highly dispersed systems) are to a considerable extent already reversible.

For systems consisting only of a few particles, however, the thermodynamic concepts, being statistical, lose their meaning. It is impossible, for instance, to speak of the pressure or entropy of a single molecule. The difference between order and disorder, and, therefore, between heat and work, vanishes for such "systems". This is why the law of the growth in entropy also loses its meaning. With an increase in the number of particles, i.e. with a transition to ordinary systems, the "most probable" becomes "authentic". In other words, the statistical nature of the second law advances

to the foreground for microsystems, while its content defined by the formulations given in the preceding section is the main one for ordinary systems.

Example 11. Do not fluctuations contradict the impossibility of designing a perpetual motion machine?

Solution. It is impossible to use fluctuations for designing a perpetual motion machine (of the second kind, since we are dealing with an isothermal process). If the presumed "micromachine" is so mobile as to respond to the action of the fluctuations in the working body, then, owing to its molecular nature, the mechanism itself will be subjected to fluctuations. The latter will randomly act first in one and then in another direction, i.e. the fluctuations in the mechanism will be absolutely uncoordinated with those in the working body. Consequently, the statement on the impossibility of a perpetual motion machine of the second kind also holds for a statistical consideration of physical systems.

4.3.5. The Invalidity of the "Theory of Heat Death" of the Universe

The first law of thermodynamics can be applied not only to finite, but also to infinitely small and great systems; the second law, however, is restricted both "from below" and "from above". In the same way that we cannot apply the principle of growth in entropy to microsystems, we also cannot extend it to processes of a cosmic scale.

The application to the Universe of thermodynamic concepts that figure in the principle of the growth in entropy is unfounded. The extrapolation of the second law to the Universe is based on a false hypothesis of the finite nature of the Universe. We cannot treat the Universe as an "isolated system"; we cannot equate the entropy of the Universe to the sum of the entropies of its separate parts. One must remember the infinite diversity of conditions in which material bodies exist in the boundless space of the Universe (from extremely low densities and extremely low temperatures to enormous velocities and gravitational fields; in these conditions processes can occur reversibly, but not infinitely slowly). The second law is a generalization of facts observed during lengths of time that cannot at all be compared with the periods during which cosmic systems appear, develop and perish, and therefore its unconditional extension to the boundless Universe is absolutely groundless. As V. Lenin noted, "any truth, if 'overdone'..., if exaggerated, or if carried beyond the limits of its actual applicability, can be reduced

to an absurdity, and is even bound to become an absurdity under these conditions."*

To consider that the entropy of the Universe tends to a maximum means to assume that as processes take place, their motive force will be exhausted and that in the long run such a state will set in when processes in the Universe terminate, i.e. heat death ensues. The absurdity and unscientific nature of this conception is obvious: it leads to the notion that the absolute destruction of separate forms of motion of matter is possible.

Thus the idealistic "theory of heat death" based on the unfounded absolutization of the second law of thermodynamics negates the eternity of motion of matter and thus denies the law of conservation and conversion of energy. The conception of heat death makes us not only believe that matter reaches a state deprived of motion, but also presume that the Universe appeared as a result of a specific creative act which formed both the Universe itself and a difference of entropies and temperatures in various parts of it. Clearly this metaphysical tenet on the absolute beginning and end of the Universe is unscientific and is incompatible with dialectical materialism.

The arbitrary nature and invalidity of the "theory of heat death" of the Universe was thoroughly criticized by F. Engels. Exposing the groundlessness of this reactionary "theory", Engels suggested finding the ways in which scattered heat is converted into different forms of energy. Indicating the qualitative indestructibility of motion, Engels concluded that "reversible" processes were inevitable. L. Boltzmann later arrived at the same conclusion. His "fluctuation hypothesis" was a simplified illustration of Engels's. Modern science, which has discovered intranuclear transformations, the transformations of particles of a field into particles of a substance and the energy of radiation into the energy of electric charges, the formation from scattered interstellar matter of stars and star associations, confirms the existence in the Universe of processes leading to a decrease in entropy.

The unscientific nature of the heat death theory also follows from relativistic thermodynamics (thermodynamics related to the general theory of relativity): for sufficiently big systems (not necessarily infinitely great!) that are in a non-stationary gravitational field, a growth in entropy does not result in the setting in of equilibrium, since the entropy grows, but does not tend to a maximum (see, for example, [A38]).

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* V. I. Lenin. *Collected Works*, Vol. 31, p. 62. Moscow, Progress Publishers, 1966.

Chapter 5

THERMODYNAMIC AND CHEMICAL POTENTIALS. THE GENERAL CONDITIONS OF EQUILIBRIUM

5.1. THERMODYNAMIC POTENTIALS

In the general case, Eq. (4.16) combining the first and second laws of thermodynamics can be written down in the form

$$T\,dS = dU + \delta W_{\max} \text{ or } -(p\,dV + \delta W'_{\max}) = dU - T\,dS \quad (5.1)$$

whence

$$\delta W'_{\max} = -dU + T\,dS - p\,dV \quad (5.2)$$

where $\delta W'_{\max}$ = **maximum useful work** *

$p\,dV$ = work done for expansion (compression) and needed to maintain the pressure p in the system at the given moment.

It follows from Eq. (5.2) that there exist *characteristic* ** *functions of state of a system whose decrease in a reversible process occurring when a definite pair of thermodynamic parameters are constant equals the maximum useful work.* By analogy with mechanics, where the work of constantly acting forces is also determined by the difference between the potentials of these forces in the initial and final states of a system independent of the path, these functions are called **thermodynamic potentials.** Four of them are distinguished, depending on the conditions in which a process occurs.

1. At V, S = const, Eq. (5.2) becomes

$$\delta W'_{\max} = -dU \quad \text{or} \quad -\Delta U = W'_{\max} \quad (5.3)$$

i.e. energy is an isochoric-isentropic potential.

2. At p, S = const, we find from Eq. (5.2) that

$$\delta W'_{\max} = -d(U + pV)$$

whence in accordance with Eq. (2.10) we have

$$\delta W'_{\max} = -dH \text{ and } -\Delta H = W'_{\max} \quad (5.4)$$

i.e. enthalpy is an isobaric-isentropic potential.

* See the footnote on p. 40.

** For an explanation of this term see p. 123.

According to their common feature (the constancy of S), the functions U and H are sometimes called isentropic potentials.

It does not at all follow from Eqs. (5.3) and (5.4) that the quantities ΔU and ΔH, which in Chapter 3 denoted heat effects, in the present chapter acquire the meaning of work, since the heat effects equal $\Delta U_{V,T}$ and $\Delta H_{p,T}$, respectively, whereas the maximum useful work (with the opposite sign) equals $\Delta U_{V,S}$ and $\Delta H_{p,S}$, respectively.

3. At V, T = const, Eq. (5.2) becomes

$$\delta W'_{\max} = -d(U - TS)$$

The quantity $(U - TS)$ is a property of a system. It is called the **Helmholtz energy** or the **isochoric-isothermal** (or simply the **isochoric**) **potential.** This function was introduced by H. Helmholtz (1882) and is denoted by A. From the expression

$$A \equiv U - TS \tag{5.5}$$

we get an equation explaining the meaning of this function: at V, T = const, we have

$$\delta W'_{\max} = -dA \quad \text{or} \quad -\Delta A = W'_{\max} \tag{5.6}$$

It can be seen that

$$\Delta A_{V,T} = \Delta U_{V,T} - (T\Delta S)_{V,T}$$

or

$$-\Delta U_{V,T} = (W'_{\max})_{V,T} - (Q_{\min})_{V,T} \tag{5.7}$$

where $\Delta U_{V,T}$ = heat effect of an isochoric process, i.e. the heat of an irreversible isochoric-isothermal process

$(T\Delta S)_{V,T} = (Q_{\min})_{V,T}$ = heat of a reversible isochoric-isothermal process.

The last quantity equals the heat which is absorbed from a thermostat (in a reversible endothermic process) or is liberated into a thermostat (in a reversible exothermic process) and by means of which the temperature is kept constant.

According to Eqs. (5.5) and (5.1), the change in the Helmholtz energy in the general case is expressed by the equation

$$dA = -\delta W_{\max} - S\,dT = -(p\,dV + \delta W'_{\max}) - S\,dT \tag{5.8}$$

from which for T, V = const we get Eq. (5.6).

Equation (5.8) can be used to find the dependence of the Helmholtz energy on temperature and volume. Thus, in the absence of non-mechanical work $\delta W'_{\max}$ we have

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \tag{5.9}$$

and

$$\left(\frac{\partial A}{\partial V}\right)_T = -p \tag{5.10}$$

Combining Eqs. (5.5) and (5.9), writing down the relationship obtained for two states of a system, and then subtracting by terms, we find that

$$\Delta A_{V,T} = \Delta U_{V,T} + T\left(\frac{\partial \Delta A}{\partial T}\right)_V \tag{5.11}$$

It is easy to see that this equation is another way to write down Eq. (5.7).

If we pass over from the condition V, T = const to the condition T = const, then it follows from Eq. (5.1) that

$$(W_{max})_T = -\Delta(U - TS)$$

or

$$-\Delta A_T = (W_{max})_T \tag{5.12}$$

i.e. *in a reversible isothermal process, the decrease in the Helmholtz energy equals the maximum work performed by the system in this process.* Thus, if a chemical reaction proceeding in a galvanic cell is being studied, then

$$-\Delta A_T = \int_1^2 p\, dV + zEF \tag{5.13}$$

where E = e.m.f. of a *reversible* galvanic cell
z = number of gramme-equivalents
F = Faraday constant.

It follows from Eq. (5.12) that when T = const only part of the internal energy transforms into work even in a reversible process. (This explains one of the synonymous terms — "free energy" *.) The other part, "bound energy" TS, is isothermally useless.

Writing down Eq. (5.5) for an isothermal transition from one state to another, we get

$$\Delta A_T = \Delta U_T - T\Delta S \tag{5.14}$$

The quantity $T\Delta S$ equals the increment of the "bound energy" in a reversible isothermal process. Indeed, in the general case $dU_{tr} = TdS + SdT$, whereas in a reversible isothermal process $TdS = \delta Q$ and $SdT = 0$, i.e. $\Delta U_{tr} = T\Delta S = Q_{rev}$. Hence, Eq. (5.13) can be written down as follows:

$$-\Delta U_T = (W_{max})_T - (Q_{min})_T \tag{5.15}$$

* This term, which was previously more widely used, but is now losing ground, has faults. Thus, it follows from Eq. (5.5) that an increase in temperature leads to a decrease in "free energy", whereas the "workability" of a system should have increased with a growing temperature.

This equation is similar to Eq. (5.7). In a reversible isothermal process, the quantity $T\Delta S = Q_{\min}$ equals the heat given up to the heat source (thermostat) by means of which a constant temperature is maintained. In this case, $\Delta S<0$, $\Delta A_T > \Delta U_T$ and $W_{\max} < \Delta U_T$. If a reversible process is endothermic, then heat, on the contrary, is taken from the source. Here $\Delta S > 0$ and $W_{\max} > -\Delta U_T$. In an endothermic process, despite the terminology, the decrease in the free energy is not a part of the decrease in the internal energy, but exceeds it (by the heat received from the heat source).

In an irreversible isothermal process, the work obtained will be less than in a reversible one, while the work spent will be greater; the decrease in the Helmholtz energy (or its corresponding increase) remains (at identical initial and final states) unchanged. For this reason, in an irreversible isothermal process we have

$$-\Delta A > W_T$$

Thus, the quantity W fluctuates within the limits determined by the inequality

$$\int_1^2 p\,dV \leqslant W \leqslant -\Delta A_T$$

For non-isothermal processes, the quantity ΔA is not a measure of work.

For an irreversible process, $W < W_{\max}$ and $Q > Q_{\min}$. Consequently, Eq. (5.15) acquires the form

$$-\Delta U = (W_{\min})_T - (Q_{\max})_T \tag{5.16}$$

The equation

$$\Delta A_T = \Delta U_T + T\left(\frac{\partial \Delta A}{\partial T}\right)_{\Delta V} \tag{5.17}$$

will be analogous to Eq. (5.11) for an isothermal process. This equation contains the subscript "ΔV", since in the general case the volumes for A_1 and A_2 may be different (but in differentiation with respect to T each one of them, and therefore also ΔV, must be constant). Indeed, for an ideal gas

$$\left(\frac{\partial \Delta A}{\partial T}\right)_{\Delta V} = -R \ln \frac{V_2}{V_1}$$

4. At p, T = const, from Eq. (5.2) we find

$$\delta W'_{\max} = -d(U + pV - TS) \tag{5.18}$$

The quantity in parentheses is a property of a system. This function was introduced by J. Gibbs (1875) and is called the **Gibbs energy.** It is denoted by the symbol G. Therefore

$$G \equiv U - TS + pV \equiv H - TS \equiv A + pV \tag{5.19}$$

A comparison of Eqs. (5.19) and (5.5) permits us to find an analogy between the functions G and A and show that quite often the change in G differs very slightly from that in A (especially for processes in condensed systems, i.e. with the participation of only solids and liquids).

From expressions (5.18) and (5.19) it follows that at p, T = const

$$\delta W'_{\max} = -dG \quad \text{and} \quad -\Delta G = W'_{\max} \tag{5.20}$$

i.e. the function G is an **isobaric-isothermal potential.** It is frequently denoted by the abbreviated term "isobaric potential".

In particular, for reactions in a galvanic cell

$$-\Delta G = zEF \tag{5.21}$$

In accordance with their common feature (the constancy of T), the functions A and G can be called isothermal potentials.

A relationship similar to Eq. (5.7) follows from Eq. (5.19):

$$\Delta G_{p,T} = \Delta H_{p,T} - (T\Delta S)_{p,T}$$

or

$$-\Delta H_{p,T} = (W'_{\max})_{p,T} - (Q_{\min})_{p,T} \tag{5.22}$$

where $\Delta H_{p,T}$ = heat effect of an irreversible isobaric-isothermal process

$(T\Delta S)_{p,T} = (Q_{\min})_{p,T}$ = heat liberated (or absorbed) in a reversible isobaric-isothermal process.

The last quantity equals the heat that is absorbed from a thermostat (in an endothermic reversible process) or is liberated into a thermostat (in an exothermic reversible process) and by means of which an isothermal nature of the process is maintained.

According to Eqs. (5.1) and (5.19), the change in the Gibbs energy is generally expressed by the equation

$$dG = -S\,dT + V\,dp - \delta W'_{\max} \tag{5.23}$$

from which for p, T = const we get Eq. (5.20). Equation (5.23) allows us to find the dependence of the Gibbs energy on temperature and pressure. Thus, in the absence of non-mechanical work $\delta W'_{\max}$, we have

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \tag{5.24}$$

and

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{5.25}$$

Combining Eqs. (5.19) and (5.24), writing down the relationship obtained for two states of a system and subtracting by terms, we find that

$$\Delta G_{p,T} = \Delta H_{p,T} + T\left(\frac{\partial \Delta G}{\partial T}\right)_p \tag{5.26}$$

It is easy to see that this equation is an altered form of Eq. (5.22).

The equations relating the functions A and G to their temperature derivatives are called **Gibbs-Helmholtz equations.** The more important ones are Eqs. (5.11) and (5.26) relating the quantities ΔA and ΔG to their temperature derivatives. They usually bear the same name, although they are only a particular case of a Gibbs-Helmholtz equation.

5.1.1. Change in Thermodynamic Potential as a Criterion of the Equilibrium and Spontaneous Nature of a Process

Since changes in U, H, A and G do not depend on the course of a process, and the work in an irreversible process is less than in a reversible one, the equation

$$-\Delta \Pi_{A,B} = W'_{\max} \tag{5.27}$$

generalizing Eqs. (5.3, 5.4, 5.6 and 5.20) will take on the following form for an irreversible process:

$$-\Delta \Pi_{A,B} > W' \tag{5.28}$$

Consequently, the limits of the change in the useful work will be determined by the inequality

$$0 \leqslant W' \leqslant -\Delta \Pi_{A,B} \tag{5.29}$$

(In all three equations the Greek letter Π denotes a thermodynamic potential, and A, B the fixed parameters corresponding to it.)

If a system is only under the action of an external pressure, i.e. can perform only mechanical work, then $W' = 0$ and Eq. (5.28) becomes

$$\Delta \Pi_{A,B} < 0 \tag{5.30}$$

i.e. *in a spontaneous process, the thermodynamic potential diminishes.* This conclusion follows from the meaning of a potential; it also holds when $W' \neq 0$. Thus, a chemical reaction proceeds as long as useful work is performed (for instance when chemical energy is converted into electrical energy).

It is also obvious that a thermodynamic potential, which diminishes during the course of a process, reaches a minimum at the

moment of equilibrium. Hence, if inequality (5.30) is a criterion of the spontaneous nature (irreversibility) of a process, then the following equation is a criterion of equilibrium in a system:

$$d\Pi_{A,B} = 0 \quad \text{or} \quad \Delta\Pi_{A,B} = 0 \tag{5.31}$$

All conceivable processes are thus covered by the relationship

$$d\Pi_{A,B} \leqslant 0 \tag{5.32}$$

The special place occupied by entropy among the various criteria is not because the use of thermodynamic potentials is limited by the constancy of definite parameters, since the use of entropy is also limited by the condition of the isolated state of a system, i.e. by the condition $\delta Q = 0$ (or $U, V = \text{const}$). The fact is that entropy is directly related to one of the basic laws of nature, and for this reason it was the first criterion of the direction of a process to be introduced into science. The notion of the quantities A and G as functions whose change also characterizes the direction of a process was adopted from the notion of entropy. Indeed, if the value of S grows, then as follows from Eqs. (5.5) and (5.19), the values of A and G diminish.

Thus, from the standpoint of interchangeability, all the criteria of equilibrium are equivalent. This holds, however, from the theoretical point of view. Matters differ somewhat in practice.

Calculations of a process with the aid of the function S are often cumbersome, since isolation of a system is needed, i.e. it is necessary to know the change in the entropy of all the bodies participating in the process (it should be remembered that the rule of the unchangeability of the entropy in a reversible process and of its growth in an irreversible one relates to isolated systems, whereas chemical reactions *always* proceed with a heat effect). This not only complicates calculations, but often makes them practically impossible because the change in the entropy of the heat source (sources) must be taken into account. This is why thermodynamic potentials rather than entropy are usually used as a criterion of equilibrium in calculations of chemical processes.

Energy and enthalpy are almost never used in calculations as *potentials*, since the conditions for their employment ($S, V = \text{const}$ and $S, p = \text{const}$, respectively) are rarely encountered in practice. The use of various diagrams (enthalpy-entropy, enthalpy-temperature, enthalpy-concentration, etc.) does not contradict what was said above, since here we do not have heat calculations in mind.

In practice, it is convenient to use p and T as independent variables in most cases, and not V and T, because many chemical and physical processes occur at a constant temperature and constant pressure (as a rule $p = 1$ atm). No isolation of a system is needed if the function G is used, since a restriction — the action of only an external pressure — is imposed on the system.

Even if a change does occur in a system that leads to the appearance of finite temperature and pressure differences within the system or between it and its surroundings, an inevitable levelling out of the temperatures and pressures will result. When taken together, these two processes are equivalent to a spontaneous change proceeding at p, T = const. In both cases, the change in the Gibbs energy will be the same. For example, in the production of sulphuric acid, the reactants (pyrite, air and water) and the product (sulphuric acid) are at the same temperature and pressure. The same can be said of the producer gas process and many others.

This is how chemical reactions differ from physical processes, since a change in volume without a simultaneous change in pressure and temperature is possible only in a chemical reaction. (Among physical processes an exception are phase transitions, i.e. transitions from one state of aggregation to another.)

Also of great significance is the circumstance that at the moment of equilibrium it is exactly p and T that become equal in all the phases of a system. This is the reason why the function G is usually preferred as a criterion of the equilibrium and spontaneous nature of processes.

5.1.2. Various Thermodynamic Relationships

The number of relationships between various quantities and parameters is very great. We have considered only a few of them (p, V, T, U, H, S, A, G, etc.).

To find other relationships, we may use a variety of means, such as N. Suvorov's table (1951) of the first derivatives (Table 5). It should be borne in mind here that the following symbols are in general use.

(a) Thermal coefficients, i.e. quantities characterizing the change in a thermal parameter depending on the change in another thermal parameter in a given thermodynamic process:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \text{isobaric cubic expansion coefficient}$$

$$\varkappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \text{isothermal compressibility}$$

$$\gamma = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V = \text{isochoric pressure coefficient.}$$

(b) Caloric coefficients:

$$l = \left(\frac{\delta Q}{\partial V}\right)_T = \text{heat of isothermal expansion}$$

$$h = \left(\frac{\delta Q}{\partial p}\right)_T = \text{heat of isothermal pressure increase}$$

Table 5. **Relationships Between Selected Quantities**

	p = const	T = const	V = const	S = const	U = const	H = const	A = const	G = const
(∂p)	—	-1	$-\alpha V$	$-C_p/T$	$\alpha pV-C_p$	$-C_p$	$S+\alpha pV$	S
(∂T)	1	—	$-\varkappa V$	$-\alpha V$	$(\varkappa p-\alpha T)V$	$(1-\alpha T)V$	$\varkappa pV$	V
(∂V)	αV	$\varkappa V$	—	$C_V\varkappa V/T$	$C_V\varkappa V$	$(C_V\varkappa+\alpha V)V$	$-\varkappa SV$	$(\alpha V-\varkappa S)V$
(∂S)	C_p/T	αV	$-C_V\varkappa V/T$	—	$C_V\varkappa pV/T$	C_pV/T	$(C_V\varkappa p-$ $-\alpha TS)V/T$	$(C_p-\alpha TS)V/T$
(∂Q)	C_p	αTV	$-C_V\varkappa V$	0	$C_V\varkappa pV$	C_pV	$(C_V\varkappa p-$ $-\alpha TS)V$	$(C_p-\alpha TS)V$
(∂W)	αpV	$\varkappa pV$	0	$C_V\varkappa pV/T$	$C_V\varkappa pV$	$(C_V\varkappa+\alpha V)pV$	$-\varkappa SpV$	$(\alpha V-\varkappa S)pV$
(∂U)	$C_p-\alpha pV$	$(\alpha T-\varkappa p)$	$-C_V\varkappa V$	$-C_V\varkappa pV/T$	—	$(C_p-$ $-\alpha pV)V-$ $-C_V\varkappa pV$	$(\varkappa Sp-\alpha TS+$ $+C_V\varkappa p)V$	$V(C_p-\alpha pV)-$ $-(\alpha TV-$ $-\varkappa pV)S$
(∂H)	C_p	$(\alpha T-1)V$	$-(C_V\varkappa+$ $+\alpha V)V$	$-C_pV/T$	$C_V\varkappa pV-$ $-(C_p-\alpha pV)V$	—	$(S+\alpha pV)\times$ $\times(V-\alpha TV)+$ $+C_p\varkappa pV$	$(C_p+S-$ $-\alpha TS)V$
(∂A)	$-(S+\alpha pV)$	$-\varkappa pV$	$\varkappa SV$	$(\alpha TS-$ $-C_V\varkappa p)V/T$	$(-C_V\varkappa p+\alpha TS-$ $-\varkappa Sp)V$	$(S+\alpha pV)\times$ $\times(\alpha TV-$ $-V)-C_p\varkappa pV$	—	$SV(\varkappa p-1)-$ $-\alpha pV^2$
(∂G)	$-S$	$-V$	$(\varkappa S-\alpha V)V$	$(\alpha TS-$ $-C_p)V/T$	$V(\alpha pV-C_p)+$ $+(\alpha TV-\varkappa pV)S$	$(\alpha TS-$ $-C_p-S)V$	$SV(1-\varkappa p)+$ $+\alpha pV^2$	X

$$\chi = \left(\frac{\delta Q}{\partial V}\right)_p = \text{heat of isobaric expansion}$$

$$\lambda = \left(\frac{\delta Q}{\partial p}\right)_V = \text{heat of isochoric pressure increase.}$$

To find the value of $(\partial x/\partial y)_z$, take the expression in the line ∂x and in the column $z = \text{const}$ and divide it by the expression in the line ∂y in the same column.

The second derivatives can be obtained by differentiating the first. It should be remembered that since W and Q are not properties of a system, then

$$\frac{\partial^2 W}{\partial y\, \partial z} \neq \frac{\partial^2 W}{\partial z\, \partial y} \quad \text{and} \quad \frac{\partial^2 Q}{\partial y\, \partial z} \neq \frac{\partial^2 Q}{\partial z\, \partial y}$$

5.2. CHARACTERISTIC FUNCTIONS

A function of state (and the partial derivatives of its various orders with respect to the variables corresponding to it) that can be used to express all the thermodynamic properties of a system in the simplest and in an explicit form is called a characteristic function.

The most widely used characteristic functions are the thermodynamic potentials and entropy. The **Planck function** $(-G/T)$, which is not a thermodynamic potential, is also a characteristic function.

The definition of characteristic functions shows the need to properly choose the corresponding variables. For instance if a process does not involve a change in composition, enthalpy is a characteristic function only at variable values of p and S. Consequently, if a number of properties are to be determined by a graph showing the change in the function H, then the coordinates H-p-S should be used. Indeed, the combination H-p-S gives any thermodynamic function. Thus, differentiation of Eq. (4.17) with respect to S and p gives, respectively, T and V. The use of the quantities T and V in Eqs. (2.10), (5.5) and (5.19) gives, respectively, U, A and G, etc. The same can be said, for example, about the combination U-V-S (see pp. 125-127), which has often been used recently with the introduction of statistical methods into classical thermodynamics. Gibbs constructed his thermodynamics on this combination.

If T is one of the variables, then A or G should be taken as the characteristic function, depending on whether V or p has been selected as the second basic parameter. It is good practice to use the function A, i.e. the relationship A-V-T when considering phase equilibria in solutions and, in particular, when interpreting them geometrically.

The functional relationship $U = \varphi(V, T)$ is not good from this standpoint — if we proceed from an equation $U = \varphi(V, T)$, then integration will be needed to determine a number of quantities, and unknown functions will therefore appear. Indeed, since $T = (\partial U/\partial S)_V$, then

$$U = \varphi\left[V, \left(\frac{\partial U}{\partial S}\right)_V\right] \quad \text{or} \quad \left(\frac{\partial S}{\partial U}\right)_V = \varphi(V, T)$$

The latter expression cannot be used to derive entropy as a function of energy and volume. As a result, the expression for entropy will contain an unknown function of volume.

Similar reasoning also holds with respect to $H = \varphi(p, T)$.

Therefore, a roundabout way had to be followed in deriving Eqs. (4.18) and (4.19). In accordance with Eqs. (1.1) and (1.5), they are directly obtained from Eqs. (5.8) and (5.23).

We have only used the relationship $U = \varphi(V, T)$ that is not successful from the standpoint of characteristic functions because volume and temperature figure most frequently in calculations. For the same reason, entropy is often considered as a function of V and T (or p and T).

In addition, the derivatives of A and G give a relationship between p, V and T, whereas the derivatives of H and U give the same equation, but now containing the variables p, V and S, which is inconvenient in practice.*

Example 1. Show that A is a characteristic function with the variables V and T.

Solution. The quantities S and p are determined from Eq. (5.8) [see Eqs. (5.9) and (5.10)]. The same equation in combination with Eq. (5.5) yields (the subscript $\delta W_{max} = 0$ has been omitted everywhere)

$$U = A - T\left(\frac{\partial A}{\partial T}\right)_V$$

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* It follows from Eqs. (4.16) and (4.18) that

$$\left[\frac{\partial(p/T)}{\partial T}\right]_V = \left[\frac{(\partial U/\partial V)_T}{T^2}\right]_V$$

or

$$\frac{p}{T} = \int \frac{(\partial U/\partial V)_T}{T^2}\, dT + \varphi(V)$$

where $\varphi(V)$ remains unknown even if we know $U = \varphi(V, T)$. To find an equation of state, it is necessary to know the relationship $U = \varphi(V, S)$, since it follows from Eq. (4.16) that $p = -(\partial U/\partial V)_S$. Consequently, if it is possible to derive energy as a function of volume and temperature from an equation of state, then the reverse task is impossible.

Combining Eq. (2.10) with Eqs. (5.8) and (5.5), we get

$$H = A - T\left(\frac{\partial A}{\partial T}\right)_V - V\left(\frac{\partial A}{\partial V}\right)_T$$

From Eqs. (5.19) and (5.10) we have

$$G = A - V\left(\frac{\partial A}{\partial V}\right)_T$$

Combining Eqs. (5.5) and (5.9) and differentiating the equation obtained with respect to T in accordance with Eq. (3.10), we get

$$C_V = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_V$$

Transformation of Eq. (3.14) with the aid of Eqs. (4.16), (4.18) and (1.8) gives

$$C_p = C_V - T\,\frac{(\partial p/\partial T)_V^2}{(\partial p/\partial V)_T}$$

Using Eq. (5.10) and the found value of C_V, we get

$$C_p = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_V - T\,\frac{(\partial^2 A/\partial T\,\partial V)^2}{(\partial^2 A/\partial V^2)_T}$$

Graphical Representation of Thermodynamic Properties. In accordance with Eq. (4.16), which is a differential equation of a surface $\varphi(U, V, S) = 0$, it is possible to plot a thermodynamic surface in the system of coordinates U-V-S (J. Gibbs).

To consider the properties of this thermodynamic surface, we shall take a certain point B (Fig. 25) on it. Hence the energy, entropy and volume corresponding to the state depicted by point B will be determined by the distance from this point to the relative coordinate planes, i.e. $U = Bg$, $S = gi$ and $V = gh$.

We draw two planes through point B, one parallel to coordinate plane UoS (plane Bfg) and the other parallel to coordinate plane UoV (plane beh).

The first section of the thermodynamic surface gives the isochor (*1*)-(*1*), and the second, the adiabat (*2*)-(*2*). Plane $Bbcd$ will be tangent to the thermodynamic surface at point B.

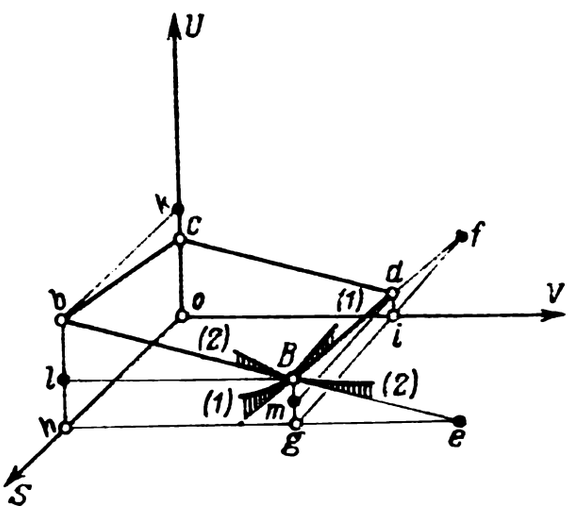

Fig. 25. Thermodynamic surface in the U-V-S system of coordinates

From the equation of the surface (4.16), it follows that $(\partial U/\partial S)_V = T$ and $-(\partial U/\partial V)_S = p$.

Therefore, tangent lines drawn through point B parallel to axes S and V form angles with plane SoV whose tangents are respectively equal to the temperature and pressure, i.e. $\tan < Bfg = T$ and $\tan < beh = p$. It follows from this that tangents drawn to a thermodynamic surface at right angles to the V-axis form angles that are identical for all the points of a given isotherm, while tangents drawn to a thermodynamic surface at right angles to the S-axis form angles that are identical for all the points of a given isobar.

The thermodynamic surface U-V-S makes it possible to graphically represent not only the energy, entropy, volume, temperature and pressure, but also to find the other thermodynamic parameters of state without any difficulty. Indeed, from the equations $Bm = \tan < Bdm \cdot md = \tan < Bfg \cdot gi = TS$ and $bl = \tan < bBl \cdot Bl = \tan < beh \cdot hg = pV$, it follows that

$$H = U + pV = Bg + bl = hl + bl = bh$$

$$A = U - TS = Bg - Bm = mg = di$$

and

$$G = H - TS = bh - Bm = ko - kc = co$$

Thus, the thermodynamic potentials H, G, A and U are expressed in the coordinate system U-V-S by perpendiculars dropped onto coordinate plane SoV from the corresponding corners of a tangent plane limited on two sides by planes SoU and UoV, and on the other two sides by planes drawn through point B in a direction parallel to these coordinate planes.

The entire above analysis also holds with respect to any figurative point on the surface. This means that the geometrical method of investigation can be used to study a variety of processes.

An advantage of this thermodynamic surface over the one in the greatest favour (p-V-T, see p. 21) is that the relationship between volume, pressure and temperature gives a less complete idea of the properties of bodies than that between volume, energy and entropy. Whereas the relationship between p, V and T is adequately determined by the relationship between V, U and S and can be obtained from the latter by differentiation, the latter relationship cannot to any extent be determined by the former. Similar reasoning can also be extended to the merits of thermodynamic surfaces in the coordinates H-p-S, U-V-T and G-p-T; this circumstance follows directly from the notion of characteristic functions.

A graph in the system of coordinates p-V-T has the practical advantage that these parameters can be measured directly; this is precisely why they are most frequently used. In addition, the system of coordinates p-V permits us to express work with the maximum simplicity (the same as the system of coordinates T-S — heat), which cannot be achieved with a combination of characteristic

functions, since neither the p-V- nor the T-S-combinations include characteristic functions with the relevant variables.

Notwithstanding this fact, the advantages of characteristic surfaces are so obvious from the thermodynamic viewpoint that all preference should be given to them. This especially relates to chemical thermodynamics, where the combination G-p-T, and less often A-V-T (for phase equilibria in solutions), is preferred to any other combination.

Surfaces similar to the one just considered have still another advantage over the surface p-V-T. While there is no general equation relating volume, temperature and pressure, the principles of thermodynamics give a general differential equation relating different characteristic functions and the variables corresponding to them.

Finally, another very important practical merit of the thermodynamic surface U-V-S is that all the quantities serving as its coordinates are additive. Consequently, surfaces constructed for different masses of a substance in the same conditions are similar to one another, and their linear dimensions are proportional to the masses which they correspond to.

Example 2. If in Fig. 25 a plane is drawn through the origin of coordinates that corresponds to the pressure and the temperature of the state depicted by point B, how will it be arranged relative to a tangent plane? What can be said about the value of the section of the vertical line confined between point B and the drawn plane? How will this section change in isobaric-isothermal processes?

Solution. The plane drawn will be parallel to tangent plane *Bbcd*. The section of the vertical line being considered will correspond to the value of the Gibbs energy for the given state. Therefore when p, $T = \text{const}$, it may either diminish or remain constant.

Example 3. How can the nature (convexity, concavity) of a thermodynamic surface U-V-S be determined? Does point B in Fig. 25 correspond to a stable or unstable state?

Solution. By Eqs. (4.16) and (4.20), we have $(\partial^2 U/\partial S^2)_V = T/C_V > 0$. For stable states, the quantity $(\partial^2 U/\partial V^2)_S$, equal by Eq. (4.16) to $-(\partial p/\partial V)_S$, is evidently also positive. Therefore, in the stable region the thermodynamic surface in the system of coordinates U-V-S will be convex-convex (downward), while in unstable regions it will be convex-concave. (We are speaking about sections that are parallel to coordinate planes SoU and VoU, respectively.) Hence, point B in Fig. 25 corresponds to a stable state of the system.

Example 4. Show that the transformation of a surface over the plane V-S to one over the planes T-V, T-p and p-S leads to the functions A, G and H, respectively.

Solution. To transform a surface U-V-S into a surface U-T-V, it is necessary to transfer the section U-V remaining unchanged

through the surface U at right angles to its axis V. Equation (4.16) in this case should change into an equation $\varphi(T, V) = Y\,dT - p\,dV$. It is obvious that $Y = -S$, since only this quantity makes $d\varphi(T, V)$ a full differential [when the latter equation is combined with Eq. (4.16)]. Therefore, $d\varphi(V, T) = dU - (T\,dS + S\,dT) = dU - d(TS)$. The integral equation $\varphi(T, V) = U - TS$ corresponds to this differential equation, i.e. by Eq. (5.5) we have $\varphi(T, V) = A$. By means of similar transformations, we find the differential equations $d\varphi(T, p) = dU - d(TS) + d(pV)$ and $d\varphi(p, V) = dU + d(pV)$ whose integration results in the functions G and H.

Other transformations do not lead to such simple and illustrative results.

5.3. CHEMICAL POTENTIAL

The main feature of any chemical reaction and of many processes in solutions is a change in the composition of the system. Therefore, to completely characterize a system, we must take into account the composition of each phase. Consequently, the use of equations with two variables, for instance Eqs. (4.16) and (4.17), corresponded to the assumption that the given system contained one or consisted of several substances between which no exchange occurred, or the amount of reacted substances was negligible in comparison with their initial amount, and therefore the composition of the system remained practically unchanged.

If we take the composition of a system as a variable, then any of the properties of each phase must be represented as a function of the number of moles of all the substances and any two of the variables p, V, T, U, H, etc.

For example $U = \varphi(V, S, n_1, n_2, \ldots)$, i.e. the total energy of a system is determined by its volume, entropy and composition, and for this reason a change in energy will depend not only on a change in volume and entropy, but also on the amount of a substance introduced into the system or removed from it. Denoting by the subscript n_j the condition of constancy of n_1, n_2, n_3, ... (i.e. of the number of moles of all the substances except substance i) and by the subscript N the composition (i.e. the number of moles of all the substances), we get

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, n_1, n_2, n_3, \ldots} dS + \left(\frac{\partial U}{\partial V}\right)_{S, n_1, n_2, n_3, \ldots} dV +$$

$$+ \left(\frac{\partial U}{\partial n_1}\right)_{V, S, n_2, n_3, \ldots} dn_1 + \left(\frac{\partial U}{\partial n_2}\right)_{V, S, n_1, n_3, \ldots} dn_2 + \ldots =$$

$$= \left(\frac{\partial U}{\partial S}\right)_{V, N} dS + \left(\frac{\partial U}{\partial V}\right)_{S, N} dV + \sum \left(\frac{\partial U}{\partial n_i}\right)_{V, S, n_j} dn_i \qquad (5.33)$$

If the composition of a system does not change, then the last term of this expression becomes equal to zero, and the entire equation transforms into Eq. (4.16).

The quantity $(\partial U/\partial n_i)_{V, S, n_j}$, i.e. the increment in the internal energy of a given phase of a system when the mass of a given substance grows by unity, if the entropy, volume and masses of all the other substances remain constant, is called the **chemical potential** (μ_i). This quantity was introduced by Gibbs (1875) and was related to a unit of mass.

To understand the meaning of this new concept, let us consider each kind of energy as the product of two quantities: (1) an **intensity factor** (intensive property), and (2) a **capacity factor** (extensive property). Thus, mechanical energy is determined by the quantity $F\,dl$, i.e. the product of the force and the increment of the distance; electrical energy — by $E\,dq$, i.e. the product of the e.m.f. and the quantity of electricity conducted; magnetic energy — by $B\,dI$, i.e. the product of the magnetic induction and the magnetization; "volume" energy — by $p\,dV$; surface energy — by $\sigma\,dA_s$, i.e. the product of the surface tension and the change in the surface area; potential energy — by $mg\,dh$; kinetic energy — by $(v^2/2)\,dm$, etc.; finally, chemical energy is determined by the quantity $\mu\,dn$.* The intensity factors are often combined under the common name of generalized forces, and the capacity factors under the name of generalized coordinates or distances. Thus, in the case of mechanical energy, the magnitude of the force will be the intensity factor

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* Extending such reasoning to heat, i.e. considering temperature as an intensity factor of "heat energy" $T\,dS$, we could call entropy its capacity factor. Such an interpretation of entropy allows us to draw the following analogy. In the same way as it is impossible, for instance, to directly measure the increase in surface area when a liquid is atomized into very fine droplets, it is also *impossible to measure* the increase in entropy, for instance in a process of reversible heating. But it is easy to calculate the change in surface area ΔA_s on the basis of the directly measured surface tension and work done for dispersion (by the equation $\Delta A_s = \int_1^2 \delta W/\sigma$), and it is just as *easy to calculate* the change in entropy ΔS on the basis of the directly measured values of Q and T (by the equation $\Delta S = \int_1^2 \delta Q/T$).

or generalized force (like p, σ, μ, etc. in the corresponding kinds of energy), while the magnitude of the distance covered (like V, A_s, n, etc.) will be the capacity factor or generalized distance showing the extent of action of the force.

Therefore, Eq. (4.16) can be written down in the general form as follows:

$$dU = T\,dS - (X\,dx + Y\,dy + \ldots) \tag{5.34}$$

where X, Y, ... = intensity factors
x, y, ... = corresponding capacity factors.

If we assume that $dx = dy = \ldots = 0$, i.e. the system is not subjected to the action of any external forces, then Eq. (5.34) becomes $dU = T\,dS$.

Thus, the intensity factors are potentials (T is the potential of "heat energy", μ, that of chemical energy, etc.), i.e. stresses (generalized forces) of the relevant kind of energy. Each time two systems with different potentials interact, levelling out of the potentials occurs because of a change in the corresponding capacity factors. For instance, the pressure levels out as a result of a change in volume, the temperature — as a result of a change in entropy, etc.

In the same way as temperature is the motive force in heat transfer, chemical potential is the motive force in mass transfer. It leads to the setting in of chemical equilibrium (and also of phase equilibrium, if mass transfer takes place in a heterogeneous system, i.e. between phases). Like other intensity factors (in the corresponding processes), the chemical potential of a substance levels out during a process, and when equilibrium sets in it becomes the same in all the coexisting phases which the given substance is in [see Eqs. (5.46)]. Thus, the amount of a substance is a chemical variable. An excessive amount of a substance compensates, as it were, for a smaller force of its chemical affinity.

Unlike other intensity factors, the chemical potential cannot be measured directly, making this concept more unclear than pressure, temperature, surface tension and the like.

Below are given equations expressing an infinitely small change in U, H, A and G for a phase whose mass and concentration may vary as a result of exchange with other phases.

If we assume that only an external pressure is acting on a system, then with the independent variables S, V and n_1, n_2, n_3, ... we get the equation

$$dU = T\,dS - p\,dV + \Sigma\mu_i\,dn_i \tag{5.35}$$

which is identical to Eq. (5.33).

With the independent variables S, p and n_1, n_2, n_3,... we have

$$dH = T\,dS + V\,dp + \Sigma\mu_i\,dn_i \tag{5.36}$$

Using T, V and n_1, n_2, n_3,... as variables, we find

$$dA = -S\,dT - p\,dV + \Sigma\mu_i\,dn_i \tag{5.37}$$

Finally, when the independent variables are p, T and n_1, n_2, n_3,..., we have

$$dG = -S\,dT + V\,dp + \Sigma\mu_i\,dn_i \tag{5.38}$$

By taking the corresponding partial derivatives, from Eqs. (5.35-5.38) we can get equations which determine the various thermodynamic parameters. From the same equations it follows that

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{V,\,S,\,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{p,\,S,\,n_j} = \left(\frac{\partial A}{\partial n_i}\right)_{V,\,T,\,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{p,\,T,\,n_j} \tag{5.39}$$

i.e. the chemical potential of a given substance equals the partial derivative of any thermodynamic potential for the given phase with respect to the number of moles of the given substance provided that the corresponding thermodynamic parameters and the number of moles of the other substances remain constant. In other words, it is a **partial molar value of a thermodynamic potential** on the condition that the corresponding parameters of state of the system remain unchanged. *

Since processes connected with a change in the composition of a system (chemical reactions, processes in solutions) are mainly studied at p, T = const, in the following we shall exclusively use the quantity $\mu_i = (\partial G/\partial n_i)_{p,\,T,\,n_j}$ and shall denote it by $\bar{G}_i$.

5.4. GENERAL CONDITIONS OF EQUILIBRIUM

Only reversible processes can take place in an equilibrium system, and this results in four very important conditions of equilibrium:

if S, V = const, then U is minimum (5.40)

if S, p = const, then H is minimum (5.41)

if V, T = const, then A is minimum (5.42)

if p, T = const, then G is minimum (5.43)

They directly follow from Eqs. (5.35)-(5.38), and each of them can be taken as the basic one.

* The quantity μ_i, in contrast to Π (here Π stands for U, H, A or G), exactly corresponds to the concept of a potential, since in accordance with its meaning a potential does not depend on the amount of a substance, whereas U, H, A and G are extensive properties.

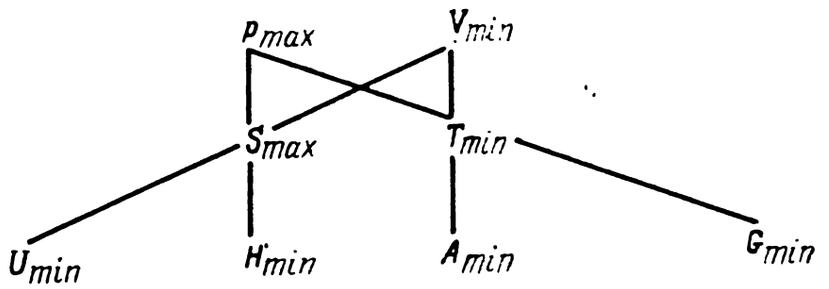
To find the conditions of equilibrium (5.31), it is necessary to determine the minimum value of a given function. Here *any variables except the fixed ones* may change in the system. Thus, if we take the Gibbs energy as a criterion of equilibrium, its minimum should be found, assuming that not temperature and pressure, but other parameters (for example the concentration) of the substances change in the system. The Gibbs energy of the system will now diminish until a minimum is reached owing to the transition of a substance from one phase to another or to chemical reactions. Similar reasoning can be applied to other cases.

We shall briefly consider conditions (5.40) and (5.41).

The first of them is known in thermodynamics as the **Gibbs postulate** (*"The energy of an equilibrium system is minimum"*). It is quite obvious that its inversion gives the criterion of equilibrium (4.9) already known from the second law, since the adiabatic condition of an isolated system is equivalent to the requirement that its energy and volume be constant while a process takes place.

Condition (5.41) corresponds to an infinitely small isobaric process in an equilibrium, thermally isolated system. This condition is not always considered, and the result is violation of the relationship between the various functions.

This relationship can be most clearly illustrated by the following diagram:



The subscripts of the parameters indicate the extreme value which the given parameter acquires in equilibrium conditions, while the lines connect the parameters which should be selected as the independent variables. Hence, in addition to the four conditions of equilibrium considered above, we get eight more. It is easy to get any of the twelve conditions on the basis of the first and second laws of thermodynamics. Their mutual equivalence follows from the equation of the partial derivatives of the characteristic functions with respect to the relevant independent variables, and also directly from Eqs. (5.35)-(5.38).

5.4.1. Stable and Unstable Equilibria

Stable equilibrium is determined by the *absolute* extremum of the corresponding functions (the absolute minimum of G at p, T =

= const, the absolute maximum of S at U, V = const, etc.). In such equilibrium, any infinitely small action (compatible with the superposed conditions) produces only an infinitely small change in the state of a system, reversal of the sign of the action calling forth reversal of the sign of the system change. The system, being brought out of the state of equilibrium, upon termination of the action tends to restore its previous state. It is also obvious that since the infinitely small action performed on the system from outside causes an infinitely small change to appear in it, the system passes over from one equilibrium state to another, neighbouring with the preceding state. Accordingly, stable equilibrium is also called **unretarded** or **true.**

By **unstable (labile) equilibrium** is meant such a state of a system when *any* infinitely small action (compatible with the superposed conditions) causes a finite change in the state of the system, i.e. an irreversible process.

Thermodynamically, this equilibrium is determined by the following conditions:

$$\text{(a)}\ dS_{V,U} = 0, \qquad d^2S_{V,U} > 0;$$
$$\text{(b)}\ dG_{p,T} = 0, \qquad d^2G_{p,T} < 0, \text{ etc.}$$

i.e. in accordance with the minimum of *all the possible* values of the entropy, the maximum of all the possible values of the Gibbs energy, etc.

If the corresponding function has a *relative* extremum, then the system is in **relative (metastable) equilibrium.** Thus, a system is relatively stable if at constant V and U it can pass over to a state with a higher value of S without in general passing through an equilibrium state, or passing through a state of unstable equilibrium. In this case, not every sufficiently small action will result in such a small change in the state of the system at which reversal of the sign of the action causes the sign of the change to reverse. Consequently, here there may also exist infinitely small actions that result in finite changes in the state of the system. The various kinds of equilibrium are shown schematically in Fig. 26.

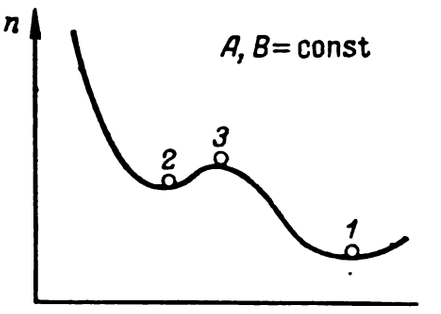


Fig. 26. Diagram showing various kinds of equilibrium: *1*—stable; *2*—metastable; *3*—unstable

Classical examples of a metastable state are the states of a supersaturated vapour, supercooled liquid or supersaturated solution. A mechanical analogue is a ball in a depression at the top or on the side of a hill.

At first glance, the possibility of the metastable state seems to be unexplainable, because the process of the decrease in G (at p, T =

= const) is always spontaneous in passing over from a metastable to a stable state. Then why does a supercooled vapour not transform into a liquid? Because retardation must be overcome to form even a small seed of the stable phase (a droplet of mist); work must be done to create a new interface between the two phases. The process of stabilization is first always attended by a growth in the Gibbs energy due to fluctuations, which lead to the appearance of particles having surplus energy. For this reason, stabilization cannot proceed spontaneously until the seeds reach a definite size or until these seeds are artificially introduced into the system, for instance in the form of electrically charged particles (overcoming retardation). Thus, a process may be attended by a growth in G. For this purpose, it is necessary for another process to occur simultaneously whose decrease in the Gibbs energy will compensate for its growth in the first process.

5.4.2. Equilibrium Coexistence of Phases. The Gibbs Phase Rule

Assume that we have a system consisting of a finite number of phases. An indispensable condition is the presence of each phase in such an amount that it would be possible to speak about its properties from the statistical standpoint and neglect the influence of the surface energy. The latter fact means that the behaviour of the substance in the boundary layer is excluded from consideration. It must be noted that the definition of a phase given in Sec. 1.2.1 is not adequate in a few cases. It will be more precise to relate this definition to **corporeal complexes** and consider **phases** as the aggregate of those complexes which have identical chemical and thermodynamic properties. For example, a mixture of crystals of right-handed and left-handed tartaric acid is a two-phase system, since its optical properties are not lost even in a solution. At the same time, left-handed and right-handed crystals of $NaClO_3$ are a single phase; in this case, the difference in properties is due not to a difference in the molecular structure and, consequently, not to different chemical properties, but to the nature of the arrangement of the molecules in a crystal. (This is why a solution of $NaClO_3$ does not rotate the plane of polarization of light.)

We shall also define the concept of a **component** or an **independent constituent.** It is customary practice to consider that the substances whose *smallest* number is essential and sufficient to form all possible phases of a given system in an equilibrium state are the components of the system. This definition leads to the following corollaries.

1. Each component can exist independently of the others (this is the reason why, for example, ions in solutions, being kinetically independent particles, are nevertheless not components).

2. The number of components N equals the number s of substances in a system if the latter do not react with one another and if the phases have a different composition. Otherwise N is less than s by the number of relationships q between the concentrations of the substances. For chemical reactions, q equals the number of *independent* reactions (see p. 138). Since the nature of interaction or reaction in a system may change, the same initially taken system may have a different number of components, depending on the conditions.

3. The chemical nature of components is of no significance for determining their number. For this reason, it makes absolutely no difference *which* substances are chosen as components. (Here we have in mind systems in which the number of components is less than that of substances.) The question of their number can be considered answered if the composition of each phase can be expressed through the concentrations of the substances that correspond to the chosen components.

Using superscripts to denote phases and subscripts to denote components, we get the following conditions for the thermodynamic equilibrium of any isolated system:

$$T' = T'' = T''' = \ldots = T^k \tag{5.44}$$

$$p' = p'' = p''' = \ldots = p^k \tag{5.45}$$

$$N \begin{cases} \mu_1' = \mu_1'', \ \mu_1' = \mu_1''', \ \mu_1' = \mu_1'''', \ldots, \mu_1' = \mu_1^k \\ \mu_2' = \mu_2'', \ \mu_2' = \mu_2''', \ \mu_2' = \mu_2'''', \ldots, \mu_2' = \mu_2^k \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \underbrace{\mu_N' = \mu_N'', \ \mu_N' = \mu_N''', \ \mu_N' = \mu_N'''', \ldots, \mu_N' = \mu_N^k}_{k-1} \end{cases} \tag{5.46}$$

Equation (5.44) — the coexisting phases have an identical temperature — corresponds to **thermal equilibrium;** Eq. (5.45) — equal pressures in all the coexisting phases — corresponds to **mechanical equilibrium;** finally, Eqs. (5.46) — each component in the coexisting phases has the same chemical potential — correspond to **chemical equilibrium.**

The validity of these equations can be proved as follows.

If in an equilibrium system δQ calories of heat pass from phase (′) to phase (″) at a constant volume and constant composition of the phases, then $dS' + dS'' = 0$, or, owing to the reversibility of the process, $-\delta Q/T' + \delta Q/T'' = 0$, i.e. $T' = T''$. Extending this reasoning to all the phases, we get Eq. (5.44).

If the condition that $T = \text{const}$ is observed, while phase (′) grows at the expense of phase (″) by the volume dV, the total volume

and composition remaining constant, then on the basis of Eq. (5.42) we have $dA' + dA'' = 0$, or $-p'dV + p''dV = 0$, i.e. $p' = p''$. When applied to all the phases, this gives us the condition of equilibrium (5.45).

Finally, if on the condition that p, $T = \text{const}$, dn_i moles of component i pass from phase (′) to phase (″), then in accordance with Eq. (5.43) we have

$$\left(\frac{\partial G'}{\partial n_i'}\right)_{p, T, n_j} dn_i' + \left(\frac{\partial G''}{\partial n_i''}\right)_{p, T, n_j} dn_i'' = 0$$

or in the general case $\Sigma \mu_i \, dn_i = 0$.

In view of the obvious equation $-dn_i' = dn_i''$, the latter condition can be written down as $\mu_i' = \mu_i''$ (or $\bar{G}_i' = \bar{G}_i''$). Extending this conclusion to all the components and all the phases, we get the condition of equilibrium (5.46).*

Thus, *equilibrium is characterized by the equality of the temperatures and pressures in all the coexisting phases of a system and by the equality of the chemical potentials (partial molar Gibbs energies) of each component in all the coexisting phases.* If a change in molecular weight occurs in a phase transition, we should speak not of the equality of the molar chemical potentials, but of the equality of the chemical potentials related to a constant unit, for instance to one gramme.

Consider a system consisting of N components, each of which is in all k phases. Let n stand for the number of parameters that are the same in all the phases of a system. Hence the total number of parameters determining the state of the system will equal n plus the number of independent concentrations, i.e. $n + k(N - 1)$, since the concentration of a component in a given phase is determined if the concentration of the remaining components is given. The number of equations (5.46) characterizing the equilibrium distribution of each component between the different phases will for each component equal the number of phase interfaces, i.e. $k - 1$, altogether $N(k - 1)$. These equations, which interrelate the chemical potentials, diminish the number of independent quantities characterizing the system by $N(k - 1)$.

The number of parameters of the phases of an equilibrium system which can take on arbitrary values *within the interval in which the number of phases does not change* is called the **variance** of the system or the **number of thermodynamic degrees of freedom of the system** (f). It will equal $n + k(N - 1) - N(k - 1)$, i.e.

$$f = N - k + n \quad \text{or} \quad f = s - q - k + n \qquad (5.47)$$

Equation (5.47) is called the **Gibbs phase rule,** although it should have been called the *law* of phase equilibrium, since a rule means

* Equations (5.46) are absolutely accurate if the system is not in a gravitational field, and Eqs. (5.44) and (5.45) — if in addition the interfaces are flat.

an approximate and particular regularity, while here we have an absolutely accurate and general relationship.

In accordance with their number of degrees of freedom, systems are divided into **invariant** ($f = 0$), **univariant** ($f = 1$), **bivariant** ones ($f = 2$), etc. In the first systems, the retaining of equilibrium requires the constancy of all the parameters; in the second ones — constancy of all the parameters except one, etc. The number of degrees of freedom can be defined differently; for example, systems whose state of equilibrium is determined if the values of any two parameters are given can be considered bivariant.

It was assumed in deriving the phase rule that all the components are in all the phases. But even if this condition is not observed, Eq. (5.47) remains valid, since the number of parameters and the number of equations decrease by the same value.

Consider, for example, a system consisting of salt and water with the maximum possible number of phases. Assume that this two-component system contains a saturated solution, vapour, ice and solid salt. Since the two components are not present in all the phases, the number of independent variables and the number of equations ought to be calculated separately for each component. In the given case, however, this is superfluous — the number of parameters equals three (pressure and temperature, which are identical in all the phases, and the concentration of the saturated solution). The number of equations (5.46) also equals three:

$$\mu^{c}_{H_2O} = \mu^{sol}_{H_2O}, \quad \mu^{sol}_{H_2O} = \mu^{g}_{H_2O} \text{ and } \mu^{c}_{salt} = \mu^{sol}_{salt}$$

(the equation $\mu^{c}_{H_2O} = \mu^{g}_{H_2O}$ is superfluous, because it is a corollary of the first two). Hence, $f = 3 - 3 = 0$, i.e. the coexistence of the four phases in a two-component system can take place at a single set of values of temperature, pressure and the concentration of the solution. Consequently, the system is invariant. The same result can be obtained in a purely formal way, namely, $N = 2$, $k = 4$, $n = 2$ (p, T), whence by Eq (5.47) we have $f = 0$. This signifies that it is sufficient to change any parameter for equilibrium to be violated and at least one of the phases to disappear.

Thus, in deriving Eq. (5.47), there is no need to assume that each component, if even in a negligible amount, is present in every phase. Moreover, such an assumption is essentially incorrect — for very small amounts of a substance, the concept of concentration may lose its meaning.

It is customary to consider systems that are under the influence of two intensity factors p and T. For such systems, Eq. (5.47) becomes

$$f = s - q - k + 2 = N - k + 2 \qquad (5.48)$$

while when p (or T) is constant, the **conditional invariance** will be

$$f_{cond} = s - q - k + 1 = N - k + 1 \qquad (5.49)$$

In conclusion we shall illustrate the phase rule with the aid of several simple examples.

1. Since $f \geqslant 0$, then $k \leqslant N + 2$. This is the reason why, for instance, it is impossible to select such values of p and T at which rhombic, monoclinic, liquid and gaseous sulphur would coexist. For the same reason, the coexistence of five phases in a two-component system is excluded.

2. If no restrictions are imposed, then $q = 0$. Thus, for the system $H_2O(lq) = H_2O(g)$ we have $f = 1 - 2 + 2 = 1$. This means that a single value of the saturated vapour pressure corresponds to each temperature. Consequently, at a fixed temperature, the saturated vapour pressure is constant, i.e. it does not depend on the volume. If we change only one of the parameters, i.e. p (at $T =$ $=$ const) or T (at $p =$ const), then equilibrium will be violated, since one of the phases vanishes. The result is an increase in the number of degrees of freedom by one, i.e. the possibility appears of simultaneously changing p and T independently of each other.

3. If chemical reactions proceed in a system, then the value of q equals the number of independent equations of the reaction. Thus, in the system

$$CaCO_3 = CaO + CO_2$$

$$q = 1 \text{ and } f = 3 - 1 - 3 + 2 = 1$$

Hence, equilibrium upon the dissociation of $CaCO_3$ is determined by a single parameter, the temperature. In other words, there is a single value of p_{CO_2} for each temperature.

4. If there is no chemical reaction, but the phases have an identical composition, then $q = s - 1$ additional relations will appear [according to the number of equations for the mole fractions $x_i' = x_i''$ written down for $(s - 1)$ substances]. For this reason, Eq. (5.47) transforms into the equation $f = 1 - k + n$, i.e. independently of the number of substances, the system will be a one-component one. The system liquid-vapour with a coinciding composition of the phases can be given as an example (see Chap. 10).

5. We shall consider the case when both restrictions are imposed. Thus, the system $NH_4Cl = NH_3 + HCl$, while similar in appearance to the preceding one ($CaCO_3 = CaO + CO_2$), differs from it in an identical composition of the phases — in both the crystalline and gaseous phases the ratio between the NH_3 and HCl is 1 : 1. Consequently, $f = 1 - 1 + 2 = 1$.

If there were an excess amount of the NH_3 or HCl in the gaseous phase (as a result of the preliminary introduction of one of the products of dissociation into the system or its partial removal from the system in the process of decomposition), then the composition

of the phases would be different, and the system would be a two-component one. Owing to the different solubility of HCl and NH_3 in liquid NH_4Cl, the same result will also be obtained upon the dissociation of molten ammonium chloride (here the difference in the composition of the phases will be insignificant because of the almost identical solubility of both gases in NH_4Cl).

Thus, in the first case the pressure of dissociation of the ammonium chloride is determined only by temperature, while in the second it depends, in addition, on the pressure of the HCl and NH_3 and on the amount of the NH_4Cl that has evaporated. Therefore, the introduction of NH_3 or HCl, or a change in the ratio $[NH_3] : [HCl]$ at a constant temperature should lead to a certain change in the pressure of dissociation of the NH_4Cl.

Naturally, if we take a mixture of NH_4Cl, NH_3 and HCl at a very low temperature, both restrictions will vanish, and $f = 3 - 3 + 2 = 2$, i.e. the possibility of an uncoordinated change (*within definite limits*) of the pressure and temperature is created without any appreciable changes in the system.

5.4.3. Principle of Displacement of Equilibrium

In concluding this chapter, we shall formulate the following rule.

If a system is in a state of equilibrium, then when forces act on it that cause violation of equilibrium, the system will pass into such a state in which the effect of the external action weakens.

This rule, called the **principle of displacement of equilibria** or the **Le Chatelier principle** (1884), reflects the circumstance that a system in which *true* equilibrium has set in is in its most natural state. The Gibbs energy (at p, T = const) can no longer diminish in it.

In the vast majority of cases, the external action consists in the supply (or removal) of energy in the form of heat, compression (or expansion) of a system, or the addition (or removal) of certain substances. Changes in temperature, pressure and concentration will be the corresponding effects of this action. Thus, when an equilibrium system is heated, changes connected with the absorption of heat appear in it. Conversely, lowering of the temperature calls forth processes attended by the liberation of heat. When the pressure on a system is increased, changes appear in it that cause a reduction in the volume of the system. Conversely, lowering of the pressure stimulates processes connected with a growth in the volume of the system.

Omitting the proof of the principle of displacement of equilibrium, which is derived from the second law of thermodynamics (see, for example [A13] and [A38]), we shall note that it indicates only the *direction* of the change in an equilibrium system. In this

respect, it is inferior to the second law and its corollaries, which make it possible to indicate not only the nature, but also the magnitude of the change. It has the advantage, however, that it permits us to immediately indicate the direction of the change without numerous additional data.

Example 5. In which direction will equilibrium be displaced in the system $H_2O(lq) \rightleftharpoons H_2O(g)$ (1) with a change in temperature, and (2) with a change in pressure?

Solution. 1. Heating should cause a process with the absorption of heat, i.e. vaporization. The violated equilibrium can be restored either by lowering the temperature to its initial value, or by changing the pressure. Since the molar volume of the liquid is less than that of the vapour, the pressure must be increased until it becomes equal to the saturated vapour pressure at the elevated temperature. In other words, the pressure of the saturated vapour increases with a growth in the temperature.

2. An increase in the pressure should cause a process connected with a decrease in the volume, i.e. condensation of the vapour. To restore the violated equilibrium, it is necessary to either lower the pressure to its initial value, or to raise the temperature to a value corresponding to the boiling point at the increased pressure. In other words, the boiling point grows with an increase in the pressure.

Example 6. How does (1) the temperature of a liquid change with an increase of its surface, and (2) the e.m.f. of a cell change with a growth in the temperature?

Solution. 1. When the surface of a liquid increases, its temperature lowers, since upon heating, the surface tension diminishes.

2. If the reaction in the galvanic cell is connected with its heating, then a growth in the temperature is attended by dropping of the e.m.f. of the cell; if, on the contrary, the flow of a current through the cell causes the latter to cool, then the e.m.f. will grow (see Sec. 13.2).

Thus, if the phase rule shows *how many parameters* determine the state of equilibrium, while the specific conditions of a problem enable one to choose these parameters, then the principle of displacement of equilibria shows how equilibrium is violated under the influence of external action. It remains to find out *by how much* the equilibrium will be shifted in connection with a *definite change* of a parameter.

Most of the following material is devoted to the solution of the latter problem as applied to various specific cases.

Chapter 6

ONE-COMPONENT HOMOGENEOUS SYSTEMS

6.1. IDEAL GAS

An ideal gas is characterized by the absence of intermolecular forces and an infinitely small volume of the molecules in comparison with the volume occupied by the gas. Its state is the limiting hypothetical state of all bodies at sufficiently low pressures and sufficiently high temperatures.

It follows from the definition that an ideal gas has only kinetic energy which does not depend on the volume. This was established experimentally: the expansion of air when it was released from the pressurized vessel in which it had been contained into an empty vessel caused no change in the temperature of the water into which both vessels were immersed. Consequently, $Q = 0$. The work also equals zero, because the volume of the system whose boundaries are considered to be the walls confining the total volume of the vessels remains unchanged. (Of course, we cannot consider that $W = 0$ on the grounds that the expanding gas does not overcome any counterpressure, since there is a vacuum only at the first moment after the valve is opened on the tube connecting the two vessels.)

Thus, according to Eq. (2.5) we have

$$\Delta U_T = 0 \quad \text{or} \quad \left(\frac{\partial U}{\partial V}\right)_T = 0 \tag{6.1}$$

i.e. in the case of an ideal gas an isothermal process is at the same time isoenergetic. Since the isothermal work done upon the expansion of a substance against an external pressure $(p\,dV)_T$ simultaneously corresponds to the work done against the molecular forces of cohesion $(\partial U/\partial V)_T dV$ [the intensity factor $(\partial U/\partial V)_T$ similar to p can be called the **internal pressure**], Eqs. (6.1) also express the fact that the internal pressure of an ideal gas equals zero.

At $T = \text{const}$, a change in V causes a change in p, therefore not only $(\partial U/\partial V)_T = 0$, but also $(\partial U/\partial p)_T = 0$. Consequently, *the*

energy of an ideal gas depends only on temperature (**Joule's law,** 1844)

$$\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_p = \frac{dU}{dT}$$

Let us see how the general thermodynamic relationships become more concrete when applied to an ideal gas.

Dividing Eq. (4.16) by dV (at T = const) and using Eq. (4.18), we get the equation

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

which in combination with Eq. (6.1) gives

$$\left(\frac{p_2}{p_1}\right)_V = \left(\frac{T_2}{T_1}\right)_V \tag{6.2}$$

It is quite obvious that

$$\left(\frac{\partial H}{\partial p}\right)_T = 0 \tag{6.3}$$

Hence Eq. (4.23) becomes

$$\left(\frac{V_2}{V_1}\right)_p = \left(\frac{T_2}{T_1}\right)_p \tag{6.4}$$

Equations (6.2) and (6.4) express the **Gay-Lussac laws** (1802).

It follows from a comparison of Eqs. (6.1) and (6.3) with Eq. (2.10) that the quantity pV depends only on temperature, hence at a given temperature

$$(pV)_T = \text{const} \tag{6.5}$$

Equation (6.5) expresses **Boyle's law** (1662), also called **Mariotte's law** (1676).

Equations (6.2), (6.4) and (6.5) can be combined in the equation

$$pV = \text{const} \cdot T \tag{6.6}$$

Since p and T are intensity factors, while V is a capacity factor, then the constant in Eq. (6.6) should be proportional to the mass of the gas, i.e. to the number of moles. Therefore for 1 mole we have

$$pV = RT \tag{6.7}$$

where R is the *molar* gas constant; on the basis of **Avogadro's law** (1811) it does not depend on the chemical nature of a gas.

At present, the equation of state of an ideal gas (6.7) is usually called the **Mendeleev-Clapeyron equation** *. The gas constant R, as can easily be seen from Eq. (6.7), numerically equals the work of expansion of 1 mole of an ideal gas upon its reversible isobaric heating by 1 K.

Combining Eqs. (2.5), (3.10), (6.1) and (6.7), we get

$$\delta Q = C_V dT + RT d \ln V \tag{6.8}$$

In accordance with Eq. (6.4) at $p = \text{const}$, the relationship between V and T is linear, hence the right-hand side of Eq. (4.24) equals zero, i.e. C_p does not depend on p. Similarly, we can show that C_V does not depend on V. Therefore, C_p and C_V are functions only of the temperature.

From Eqs. (3.14), (6.1) and (6.7) we find that

$$C_p - C_V = R \tag{6.9}$$

If we ignore the volume of solids and liquids in chemical processes, then Eq. (3.1) becomes

$$Q_p = Q_V + \Delta nRT \tag{6.10}$$

where Δn is the change in the number of moles of the gaseous reagents.

Equation (3.1) is generally used in exactly this form.

Mixtures of Ideal Gases. ** In industry, mixtures of gases are often used that are under such a small pressure that the interaction between their molecules may be disregarded (excluding chemical reactions), i.e. it may be assumed that the components of a mixture behave independently of one another. Such mixtures are called **ideal.** The gas mixtures of a number of chemical production processes, flue and blast-furnace gases, air, the exhaust gases of internal-combustion engines and many others may be included among them.

Mixtures of ideal gases are characterized by the additivity of the partial pressures and partial volumes.

The **partial pressure** *of a component of a gas mixture is the pressure which this gas entering the mixture would have if the remaining gases were removed from it, on the condition that the initial volume and temperature are retained. By the* **partial volume** *is meant the volume which a gas entering a mixture would have if the remaining gases were removed*

* Equation (6.7) was known as the Clapeyron equation. As V. Kireev established, however, B. Clapeyron introduced the equation for the total amount of a gas, and it therefore contained individual constants depending on the quantity and kind of the gas, while Eq. (6.7) relating to one mole was derived by D. Mendeleev in 1874.

** Although this section treats multi-component systems, it is expedient to consider certain properties of mixtures in the present chapter, since they directly follow from the properties of pure gases.

*from it, on the condition that the initial pressure and temperature are retained.**

The additivity of the partial pressures is expressed by **Dalton's law** (1805)

$$p = p_1 + p_2 + p_3 + \ldots \tag{6.11}$$

where p is the total pressure, and p_1, p_2, p_3,... are the partial pressures of the relevant components.

The additivity of the partial volumes is expressed by **Amagat's law** (1893)

$$V = V_1 + V_2 + V_3 + \ldots \tag{6.12}$$

where V is the total volume of the mixture, and V_1, V_2, V_3,... are the partial volumes of the relevant components.

The Mendeleev-Clapeyron equation holds for each component of a mixture of ideal gases. Consequently, using the values $p_i = n_i RT/V$ in Eq. (6.11), we get an equation of state of a mixture of ideal gases

$$p = \frac{(n_1 + n_2 + n_3 + \ldots)RT}{V} \tag{6.13}$$

or

$$p_i = px_i \tag{6.14}$$

i.e. *the partial pressure of a component of a mixture of ideal gases equals the total pressure multiplied by the mole fraction of the component.*

Combining Eq. (6.7) with Eq. (6.12), in a similar way we get

$$V = \frac{(n_1 + n_2 + n_3 + \ldots)RT}{p} \tag{6.15}$$

whence

$$V_i = Vx_i \tag{6.16}$$

i.e. *the partial volume of a component of a mixture of ideal gases equals the total volume multiplied by the mole fraction of the component.*

The additivity of the properties of a mixture of ideal gases also extends to heat capacity and enthalpy. The formation of a mixture of ideal gases from the pure substances which are at an identical

* The concepts of "partial pressure" and "partial volume" can be illustrated as follows. Assume that all the gases except one are removed from a mixture at T, V = const. The pressure in the system will therefore become equal to the partial pressure of the remaining gas. If this gas is then isothermally compressed, the volume which is obtained when the total (initial) pressure is reached will eqaul its partial volume.

temperature is not attended by any heat effect. Here equality of the initial pressures is not an essential condition, since for ideal gases H does not depend on p.

The heat effect in the formation of a mixture equals zero, while according to Eq. (6.12), the volume of the mixture equals the sum of the volumes of the components. It follows from the above and also from Eq. (2.11) that the energy of a mixture is additively composed of the energies of the components. This permits us to write down Eq. (4.16) in the form

$$dS = \frac{\Sigma dU_i + \Sigma p_i\, dV}{T}$$

Since at the same time

$$dS_i = \frac{dU_i + p_i\, dV}{T}$$

then

$$dS = \Sigma dS_i \quad \text{or} \quad S = \Sigma x_i S_i$$

(the integration constant of the last equation equals zero). It follows from Eq. (4.19) that

$$S_i = S_i^\circ - R \ln p_i \tag{6.17}$$

where S_i° is the molar entropy of a component taken in the pure state at the given temperature and at $p_i = 1$ atm.

In accordance with Eq. (4.18), we get

$$S_i = S_i^\circ + R \ln V_i \tag{6.18}$$

where S_i^* is the molar entropy of a component taken in the pure state at the given temperature and at $V_i = 1\ \text{cm}^3$.

Thus, to calculate the entropy of a component of a mixture of ideal gases, we can use Eq. (4.19) or (4.18), except that p_i has to be substituted for p, V_i for V, S_i for S and n_i for n.

It should be borne in mind that $S \neq \Sigma x_i S_i^\circ$. The difference $S - \Sigma x_i S_i^\circ$ will equal the change in entropy when the gases are mixed (ΔS upon the diffusion of each component from V_i to ΣV_i). The latter does not depend on the nature of the gases and is determined only by their concentration. The change in entropy, however, when two portions of the same gas are mixed, will equal zero (**Gibbs's paradox** — see [A4] and [A20]).

Example 1. 1. Use Eqs. (6.7), (6.8) and (6.9) to find the **equation of an adiabat** for an ideal gas. 2. How should two curves depicting an adiabatic and an isothermal processes be arranged relative to each other in the coordinates p-V?

Solution. 1. For an adiabatic process, Eq. (6.8) becomes $R\,d \ln V = -C_V\,d \ln T$, or after integration $TV^{R/C_V} = \text{const}$, whence by Eqs. (6.7) and (6.9) we get $pV^k = \text{const}$, where the **adiabatic exponent** $k = C_p/C_V$.

This equation is not precise even for an ideal gas, since when deriving it the integration was performed on the assumption that $k = \text{const}$, although $k = (1 + R/C_V)$ diminishes with a growth in temperature.

2. Adiabatic expansion, in contrast to isothermal expansion, is attended by cooling, adiabatic compression by heating.*

Consequently, an adiabat of expansion in the system of coordinates p-V will be lower than an isotherm of expansion; conversely, an adiabat of compression will be higher than the isotherm. In other words, adiabats are steeper than isotherms. [This also follows directly from a comparison of the equations (6.5) ($T = \text{const}$) and $pV^k = \text{const}$ ($\delta Q = 0$).] Consequently, if it is necessary to expand or compress a gas from a given initial volume to a given final one, it is more profitable to conduct the process isothermally, and not adiabatically, although in an isothermal process no energy of the gas is liberated for conversion into work, and the gas is only an intermediary in the conversion of heat supplied from outside into the work of expansion.

Example 2. A vessel filled with hydrogen whose pressure is kept constant contains a palladium vessel filled with nitrogen. The vessel is connected to a pressure gauge. It is known that palladium is permeable to hydrogen and impermeable to nitrogen. What will happen when the palladium vessel is heated?

Solution. When the palladium vessel is heated, hydrogen will diffuse into it until the pressure of the hydrogen inside the vessel becomes equal to the pressure outside it; the pressure gauge will show the total pressure.

Example 3. A gas consisting of 5.5% of CO_2, 35.7% of CO, 36.2% of H_2 and 22.6% of N_2 (by volume) is fed into a saturation tower where it is saturated with water vapour; it then leaves the tower at 90 °C and 760 mm Hg. Calculate the volume and composition of the gas leaving the tower and the mass of the water carried off per 100 m^3 of the gas fed in for saturation if the relative humidity of the outgoing gas is 0.85.

Solution. One hundred cubic metres of the gas contain $(0.055 \times \times 10^5)/22.410 = 246$ moles of CO_2, 1592 moles of CO, 1615 moles of H_2 and 1008 moles of N_2, i.e. a total of 4461 moles. For $t = 90$ °C

* It should be noted in passing that a change in the state of an ideal gas at a constant temperature is an example of a process when the "heat content" changes with a constant enthalpy (in expansion $Q > 0$, in compression $Q < 0$).

we have $p^{\circ}_{H_2O} = 526$ mm Hg (from the relevant table in a reference book). Hence, in the outgoing gas $p_{H_2O} = 0.85 \times 526 = 447$ mm Hg and in accordance with Eq. (6.11) we have $p_{gas} = 760 - 447 = 313$ mm Hg. Consequently, there will be $447/313 = 1.428$ m^3 or $1.428 \times 4461 \times 18/(100 \times 1000) = 1.147$ kg of vapour. The volume of the mixture after saturation will be $100 + 142.8 = 242.8$ m^3; the outgoing gas will have the composition $(5.5 \times 100)/242.8 = 2.3\%$ of CO_2, 14.7% of CO, 14.9% of H_2, 9.3% of N_2 and 58.8% of H_2O.

Example 4. Nitrous gases consisting of 132 g of NO, 115 g of O_2, 980 g of N_2 and 125 g of H_2O are contained in a volume of $V = 0.155$ m^3 at 30 °C. Find the partial pressures of the mixture components.

Solution. The total number of moles is

$$\Sigma n_i = \frac{132}{30} + \frac{115}{32} + \frac{980}{28} + \frac{125}{18} = 50$$

The composition in mole per cent is

$$\frac{132 \times 100}{30 \times 50} = 8.8\% \text{ of NO, } 7.2\% \text{ of } O_2, \ 70.1\% \text{ of } N_2 \text{ and } 13.9\% \text{ of } H_2O$$

By Eq. (6.13), the total pressure is

$$p = \frac{50 \times 82.06 \times 303.2}{0.155 \times 10^6} = 8.03 \text{ atm}$$

and the partial pressures $p_{NO} = px_{NO} = 8.03 \times 0.088 = 0.706$, $p_{O_2} = 0.577$, $p_{N_2} = 5.622$ and $p_{H_2O} = 1.115$ atm.

Example 5. Derive an equation expressing the change in the entropy of an ideal gas as a function of two variables, taking p, V and T as these variables in turn.

Solution. Combining Eqs. (4.6) and (6.8), after integration we get

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \qquad \text{(a)}$$

This equation in combination with Eq. (6.7) gives

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{RT_2/p_2}{RT_1/p_1} = C_V \ln \frac{T_2}{T_1} + R \ln \frac{T_2}{T_1} -$$

$$- R \ln \frac{p_2}{p_1} = (C_V + R) \ln \frac{T_2}{T_1} + R \ln \frac{p_1}{p_2}$$

which in accordance with Eq. (6.9) leads to

$$\Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{p_1}{p_2} \qquad (b)$$

Finally, writing down the last equation in the form

$$\Delta S = C_p \ln \frac{p_2 V_2}{p_1 V_1} + R \ln \frac{p_1}{p_2} = C_p \ln \frac{p_2}{p_1} + C_p \ln \frac{V_2}{V_1} - R \ln \frac{p_2}{p_1}$$

taking into account Eq. (6.9), we get

$$\Delta S = C_V \ln \frac{p_2}{p_1} + C_p \ln \frac{V_2}{V_1} \qquad (c)$$

Example 6. Two vessels having the same capacity are separated from each other by means of a cock. One vessel contains one mole of an ideal gas, the other is empty. Using the results obtained in the preceding example, find ΔS in the process that will occur after the cock is opened and show that the constant in Eq. (4.26) equals the Boltzmann constant, i.e. the ratio between the molar gas constant and the Avogadro constant.

Solution. Since the process is isothermal, according to Eq. (a) of Example 5 we have

$$S_2 - S_1 = R \ln \frac{V_2}{V_1} = R \ln 2$$

At the same time by Eq. (4.26) we obtain

$$S_2 - S_1 = \text{const} \ln P_2 - \text{const} \ln P_1 = \text{const} \ln \frac{P_2}{P_1}$$

or owing to the proportionality of P and the mathematical probability P_{math} we get

$$S_2 - S_1 = \text{const} \ln \frac{(P_{\text{math}})_2}{(P_{\text{math}})_1}$$

Since the mathematical probability of each molecule being in either vessel is $\frac{1}{2}$, the probability of all the molecules being in one vessel, i.e. $(P_{\text{math}})_1$, equals $\left(\frac{1}{2}\right)^{N_A}$. The probability of equal distribution of the molecules, i.e. $(P_{\text{math}})_2$, equals 1. Hence $S_2 - S_1 = \text{const} \ln 2^{N_A} = \text{const}\ N_A \ln 2$, which in comparison with the previously found value of $S_2 - S_1 = R \ln 2$ gives const $= R/N_A = k$.

Example 7. Find ΔS in the process of condensation of supercooled water vapour if $t = 25\,^\circ\text{C}$ and $p = 1$ atm. Assume that the value

of $(\partial V/\partial T)_p = 0.004\,644$ for H_2O(lq) at 25 °C and that water vapour is an ideal gas.

Solution. Since the vapour is supercooled, its condensation will be an irreversible process. Hence, to find ΔS, we mentally conduct the condensation reversibly. For this purpose, we isothermally expand the water vapour in equilibrium from atmospheric pressure (p_1) to the saturated vapour pressure at $t = 25$ °C (p_2) and then condense it:

$$\begin{array}{ccc} H_2O\ (g,\ t = 25,\ p = 1) & \xrightarrow{\Delta S = ?} & H_2O(lq,\ t = 25,\ p_2 = 0.031\,26) \\ \downarrow \Delta S_1 & & \uparrow \Delta S_2 \\ H_2O(g,\ t_1 = 25,\ p_2 = 0.031\,26) & \longrightarrow & \end{array}$$

Using Eqs. (4.8), (4.19) and (6.7), we find

$$\Delta S = \Delta S_1 + \Delta S_2 = -R \ln \frac{p_2}{p_1} + \frac{(\Delta H_{cond})_{298}}{298.2} =$$

$$= -4.576 \log \frac{0.031\,26}{1} + \frac{-10\,480}{298.2} = 6.886 + (-33.144) = -28.258$$

This process can also be conducted along a different indirect reversible path, namely, (1) heating of the water vapour at $p_1 = 1$ atm from $t_1 = 25$ to $t_2 = 100$ °C; (2) condensing of the vapour into water; (3) cooling of the water to $t = 25$ °C; and, finally, (4) reducing of the pressure over the water from $p_1 = 1$ to $p_2 = 0.031\,26$ atm:

$$\begin{array}{ccccc} H_2O(g,\ t_1 = 25,\ p_1 = 1) & & \xrightarrow{\Delta S = ?} & & H_2O(lq,\ t_1 = 25,\ p_2 = 0.031\,26) \\ \downarrow \Delta S_1' & & & & \uparrow \Delta S_4' \\ H_2O(g,\ t_2 = 100,\ p_1 = 1) & \xrightarrow{\Delta S_2'} & H_2O(lq,\ t_2 = 100,\ p_1 = 1) & \xrightarrow{\Delta S_3'} & H_2O(lq,\ t_1 = 25,\ p_1 = 1) \end{array}$$

It is obvious that $\Delta S = \Delta S_1' + \Delta S_2' + \Delta S_3' + \Delta S_4'$, or in accordance with Eqs. (4.8, 4.19 and 4.21)

$$\Delta S = \int_{298}^{373} (C_p)^g_{H_2O} \frac{dT}{T} + \frac{(\Delta H_{cond})_{373}}{373.2} + \int_{373}^{298} (C_p)^{lq}_{H_2O} \frac{dT}{T} + \int_{1}^{0.031\,26} \left[\left(\frac{\partial V}{\partial T}\right)_p\right]^{lq}_{H_2O} dp$$

Since calculations along this path should give a result coinciding with that found previously, we shall take advantage of this to find one of the quantities entering this sum. We shall calculate, for example, the heat of vaporization of water at $t_2 = 100$ °C.

Disregarding the last term of the equation and inserting into the equation used for calculations the value of $(C_p)^g_{H_2O} = 8.22 + 0.15 \times \times 10^{-3}T + 1.34 \times 10^{-6}T^2$ (see Table 4), we get $-28.258 = 1.897 +$

$+ (\Delta H_{cond})_{373}/373.2 + (-4.049)$, whence $\Delta H_{cond} = -9745$ cal/mol, or $\Delta H_{vap} = 9745$ cal/mol, which differs from the tabulated value by 0.4%.

6.2. EQUATIONS OF STATE OF A REAL GAS

In 1749 M. Lomonosov in his "Additional Reflections on the Pressure of Air" * established "...that the densities of air upon great compressions are not proportional to its pressures" and explained this fact by the finite dimensions of the particles. After this, however, for several decades it was considered unquestionable that a decrease in volume is proportional to an increase in pressure. Only at the end of the 18th century was it found that some gases can be compressed more than air, and are capable of becoming liquefied when the pressure is increased. The transformation of gases into liquids was not provided by the theory of the ideal gaseous state.

An analysis of experimental material shows that even in normal conditions calculations by Eq. (6.7) for certain gases (for example for higher hydrocarbons) give a deviation of 2 or 3%; for very high pressures, the errors become quite significant (at $p = 500$ atm they reach 600%).** Hence, the widespread use of Eq. (6.7) is explained not so much by the closeness of the real state of gases to the ideal one as by the simplicity of the equation, and also by the absence of data needed for calculations by more accurate equations.

The task of describing the properties of a real gas would have been solved if an equation of state were available that would give identical accurate results within any interval of pressures and temperatures. Thermodynamics, however, cannot supply such an equation.

The only theoretically substantiated equation is

$$pV = RT\left(1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots\right)$$

where B, C, D,... are the second, third, fourth, etc. **virial coefficients.**

These coefficients depend only on temperature. They are calculated on the basis of laws of statistical mechanics, which make it possible to obtain general equations for calculating the virial coefficients reflecting double (B), triple (C), quadruple (D), etc. inter-

* In the first half of the 18th century the only known gas was air.

** These deviations should be distinguished from those due to the association of molecules (for instance of NO_2 into N_2O_4), which sometimes reach very high values even at insignificant pressures. In the majority of cases, the association of molecules can be taken into account by an equation of state for an ideal gas (see Chap. 13).

action of gas particles. The calculations are based on equations establishing the relationships between the energy of interaction of molecules, the distance between them and their arrangement. It was established that for low pressures the coefficient B is greater than C, that the latter grows with increasing pressure, etc.

For a comparatively low pressure (lower than approximately $0.5p_{cr}$), we can limit ourselves to the second virial coefficient, i.e. use the equation $pV = RT(1 + B/V)$, which takes into consideration only double collisions.* This is the most favoured equation. The values of B for many gases are tabulated and are expressed in the form of a polynomial $B = \varphi(T)$.

If not only B, but also C is taken into account, the equation of state gives satisfactory results up to p_{cr} (at $T > T_{cr}$).

The virial equation of state, which is the only theoretically substantiated equation of state for real gases, has not found broad application both owing to the complications involved in determining its coefficients and as a result of the fact that only the second virial coefficient can be determined with a small error (for this purpose a p-V-T-relationship often has to be used).

At present over 150 equations of state proposed by different scientists are known.** Some of these equations are based on theory, but the majority of them have been found as a result of the mathematical processing of experimental data. Many empirical equations were derived for definite substances (most of them are for H_2O, and also for CO_2, NH_3, etc.). Several equations of state are given below.

In 1871 J. van der Waals proposed the equation

$$p + \frac{a}{V^2}(V - b) = RT \qquad (6.19)$$

to characterize not only the change in the state of a gas, but also of a liquid. Quantitatively, however, this equation does not always correspond to experimental data. It is better shown by isobars instead of isotherms. In addition, the values of the constants a and b in ordinary conditions are equal to about one-half of the values calculated from the critical parameters. Equation (6.19) is not suitable for high pressures.

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* In this case the relationship mentioned (for spherical molecules) has the form $B = 2\pi N_A \int_0^\infty [1 - \exp(-E_p/kT)]\, r^2\, dr$ (where r is the mean distance between the molecules and E_p is the potential energy expressed as a function of r).

** A special monograph [B113] was devoted to the equations of state of a real gas and contains a summary of the proposed equations.

D. Berthelot (1903) modified Eq. (6.19) to obtain greater accuracy, assuming that the constant a in this equation is inversely proportional to temperature. The equation he proposed is most frequently written down as follows:

$$pV = RT\left[1 + \frac{9pT_{cr}}{128p_{cr}T}\left(1 - 6\frac{T_{cr}^2}{T^2}\right)\right] \tag{6.20}$$

where p_{cr} and T_{cr} are the critical pressure and temperature (they are given for selected substances in Table 9). This equation holds for comparatively low pressures and is widely used in the calculation of various properties if corrections must be introduced for the deviation of a gas from the ideal state (see p. 484).

The Beattie-Bridgeman equation (1927)

$$pV^2 = RT\left[V + B_0\left(1 - \frac{b}{V}\right)\right]\left(1 - \frac{c}{VT^3}\right) - A_0\left(1 - \frac{a}{V}\right) \tag{6.21}$$

is of considerable practical interest. Its constants for a number of gases are given in Table 6. This equation is sometimes written down as follows:

$$p = \frac{RT}{V} + \frac{\beta}{V^2} + \frac{\gamma}{V^3} + \frac{\delta}{V^4} \tag{6.22}$$

where

$$\beta = RTB_0 - A_0 - \frac{Rc}{T^2}$$

$$\gamma = -RTB_0b + A_0a - \frac{RB_0c}{T^2}$$

$$\delta = \frac{RB_0bc}{T^2}$$

Equation (6.21) sufficiently well characterizes the compressibility of gases and can therefore be used to calculate the values of p-V-T within a broad range of values of p and T.

For very high pressures and temperatures (p/p_{cr} and T/T_{cr} equal or exceed 3), the compressibility of gases can be expressed with the aid of the simple equation

$$pV = A + Bp + CT \tag{6.23}$$

corresponding to a linear nature of the isotherms $pV = \varphi(p)$ (see Fig. 31) and the isobars $pV = \varphi(T)$. It was proposed by A. Rozen (1945), who checked it on six gases. The deviation from experimental data was 0.15-2.2%.

Table 6. **Constants of Equation of State (6.21) for Selected Gases ***

Gas	A_0	$a \times 10^3$	$B_0 \times 10^3$	$b \times 10^3$	$c \times 10^{-4}$	Interval of temperatures, °C		p_{max}, atm	V_{min}, cm³/mol
						from	to		
Ar	1.2907	23.28	39.31	0.0	5.99	−150	400	114	167
He	0.0216	59.84	14.00	0.0	0.0040	−252	400	102	100
Kr	2.4230	28.65	52.61	0	14.89	0	300	415	—
Ne	0.2125	21.96	20.60	0.0	0.101	−217	400	106	118
H_2	0.1975	−5.06	20.96	−43.59	0.0504	−244	200	103	100
H_2**	0.12404	56.18	20.22	−7.22	2.00	−70	300	1000	65
H_2***	0.12404	56.18	17.50	−19.68	2.00	−70	300	1000	37
N_2	1.3445	26.17	50.46	−6.91	4.20	−149	400	134	182
O_2	1.4911	25.62	46.24	4.21	4.80	−117	100	103	111
NH_3	2.3930	170.31	34.15	191.12	476.87	−35	325	130	340
CO	1.3445	26.17	50.46	−6.91	42.00	—	—	—	—
CO_2	5.0065	71.32	104.76	72.35	66.00	0	100	111	182
CF_2Cl_2	23.7	305	590	622	0	30	126	18.5	1.430
CH_4	2.2769	18.55	55.87	−15.87	12.83	0	200	243	167
C_2H_4	6.1520	49.64	121.56	35.97	22.68	0	200	286	125
C_2H_6	5.8800	58.61	94.00	19.15	90.00	25	250	193	200
C_3H_8	11.9200	73.21	181.00	42.93	120.00	97	275	305	100
iso-C_4H_8	16.9600	108.60	242.00	87.50	250.00	150	250	250	111
n-C_4H_{10}	17.7940	121.61	246.20	94.23	350.00	150	300	118	280
C_5H_{12}, neopentane	23.3300	151.74	335.60	133.58	400.00	—	—	—	—
n-C_7H_{16}	54.520	200.66	708.16	191.79	400.001	275	350	315	200
CH_3OH	33.309	92.46	603.62	99.29	32.03	—	—	—	—
$N_2 + 3H_2$**	3.000	21.36	25.03	−15.16	16.00	—	—	—	—
$N_2 + 3H_2$***	3.489	28.56	21.42	−30.58	16.00	—	—	—	—
Air	1.3012	19.31	46.11	−11.01	4.34	−145	200	177	125

* In calculating the constants, the volume of the gas was expressed in dm³.
** Below the critical density.
*** Above the critical density.

Below are given the values of pV/pT for nitrogen at 0 °C and 1000 atm calculated according to various equations (the observed value of $pV/pT = 2.0685$):

Equation	(6.7)	(6.19)	(6.20)	(6.21)	(6.23)
pV/pT	1.000	2.442	1.650	2.010	2.045

Although these results show that some of these equations may be used, they cannot lead to any general conclusions, because they relate to a single gas taken in one randomly chosen state.

Care should be taken in performing calculations according to any of the equations, since for each gas there is a definite and quite different interval of pressures and temperatures beyond whose limits the given equation may result in considerable errors. For example Eq. (6.21), as stated by its authors, gives good coincidence with experimental results (deviations within 0.16 to 0.18%) only up to pressures of the order of magnitude of 100 atm.

As a rule, the greater the accuracy required from equations of state, the more complicated and inconvenient they are. The following is an example of such an equation:

$$pV = RT(1 + BV^{-1} + CV^{-2} + DV^{-4} + EV^{-6} + FV^{-8})$$

It contains 25 constants, since each of the coefficients of the equation, in turn, is expressed by a polynomial of the form

$$B = b_1 + b_2T^{-1} + b_3T^{-2} + b_4T^{-4} + b_5T^{-6}$$

Any of the equations of state is an *interpolation* one, i.e. it can be used within the range of temperatures and pressures which it is recommended for. Even within this interval, however, the most reliable equations are not always sufficiently accurate for calculating *various properties of a gas*. For instance, Eq. (6.21) cannot be considered satisfactory for calculating $C_p = \varphi(p)$, because the quantity $(\partial^2V/\partial T^2)_p$ may differ considerably from the true value of this derivative. Equation (6.23) in general gives no second derivatives, since it follows from it that $(\partial^2V/\partial T^2)_p = 0$.

Example 8. Use Eq. (6.19) to find the volume of a reservoir for carbon dioxide which should contain 1 kg-mol of the gas at $p = 50$ atm and $t = 100$ °C if the constants a and b equal 3.604×10^6 and 42.8, respectively.

Solution. The simplest way to perform the calculations is by trial and error. We shall use Eq. (6.7) for orientation, whence $V = (82.06 \times 373.2)/50 = 612.5$ cm³/mol.

Inserting the found value of V into Eq. (6.19), we get $p = 44.2$, which is considerably lower than the given pressure. Using lower values of V, we find that $p = 50$ at $V \approx 530$ cm³/mol. Hence, the

volume of the reservoir for 1 kg·mol of the gas should equal $530 \times 1000 = 530\,000$ cm³ or 530 dm³.

Since the experimentally found value is $V = 513$ dm³, the actual pressure in the reservoir will be somewhat lower than the required one.

Mixtures of Real Gases.* The variety of compositions of gas mixtures and the temperature and pressure intervals used in industry are so great that it is impossible to obtain exhaustive data from the relationship p-V-T-x even for the technically most important mixtures. This is why the prediction of p-V-T-x-relationships for mixtures, particularly according to p-V-T-data for the corresponding pure gases, is so important.

Equations (6.14) and (6.16) for greatly compressed mixtures are *incompatible* and incorrect. Real gases cannot simultaneously follow both equations: the latter become independent. Thus, the properties of the mixture Ar-C_2H_4 are satisfactorily described by Eq. (6.14), whereas the properties of a nitrogen-hydrogen mixture are well described by Eq. (6.16). Equation (6.12) more often corresponds to experimental data than Eq. (6.11).

The combination of Eqs. (6.14) and (6.17) for greatly compressed gases gives unsatisfactory results; the compressibility of a mixture can be found by combining Eq. (6.11) with various equations of state of pure gases in the general form by the equation $p = \Sigma\varphi_i(T, V, x_i)$ [where $\varphi_i(T, V, x_i)$ equals the pressure which the component would have for which the given equation of state holds at the temperature and molar volume of the mixture]. Thus, considering it possible to use Eq. (6.19), we get

$$p = RT\Sigma\frac{x_i}{V - x_i b_i} - \frac{1}{V^2}\Sigma a_i x_i^2 \qquad (6.24)$$

Similar equations can be found by combining Eq. (6.11) with Eqs. (6.20), (6.21), etc. None of these equations is highly accurate owing to the inaccuracy of the initial equations, and also because of the fact that the interaction of different molecules was not taken into consideration.

It is also possible to use for calculations the equation obtained by combining Eq. (6.12) with the corresponding equation of state of a real gas. In this case, the value of $\varphi_i(p, T)$ from an equation of state of a real gas is inserted into the equation

$$V = \Sigma x_i \varphi_i(p, T)$$

for each component. This procedure is more complicated, because the calculations are based on choosing values of the partial volumes

* See the second footnote on p. 143.

of the components which, while satisfying Eq. (6.12), would also give coinciding values of the pressure (it is exactly this pressure that will be the necessary quantity at the given volume of the mixture) when introduced into the chosen equation of state of the pure gas.

A number of equations based on special methods of combining the constants of equations for pure gases have also been proposed.

For example, on the basis of Eq. (6.21), J. Beattie (1929) recommended the equation

$$p = \frac{RT}{V^2}\left(1 - \frac{c_m}{VT^3}\right)\left[V + (B_0)_m\left(1 - \frac{b_m}{V}\right)\right] - \frac{(A_0)_m}{V^2}\left(1 - \frac{a_m}{V}\right) \quad (6.25)$$

whose coefficients are

$$\left.\begin{aligned} (A_0)_m = \left[\Sigma x_i \sqrt{(A_0)_i}\right]^2, \quad a_m = \Sigma x_i a_i, \quad (B_0)_m = \Sigma x_i (B_0)_i, \\ b_m = \Sigma x_i b_i \text{ and } c_m = \Sigma x_i c_i \end{aligned}\right\} \quad (6.26)$$

The expediency of using Eq. (6.25) is due primarily to the fact that the constants of Eq. (6.21) are known for many technically important gases (see Table 6). The calculations require much time, however, and are sufficiently reliable only up to pressures of the order of magnitude of 300 to 500 atm.

Another useful equation is that proposed by E. Bartlett (1927):

$$p = p_1^\circ x_1 + p_2^\circ x_2 + \ldots \quad (6.27)$$

where p, p_1°, p_2°, ... are taken for the same temperature and the same molar volume, equal to the molar volume of the mixture.

Equation (6.27) can be considered as a modified form of Eq. (6.11). Both equations become identical for a mixture of ideal gases.

I. Krichevsky and Ya. Kazarnovsky (1939) proposed the equation of state

$$p = p_1^\circ x_1 + p_2^\circ x_2 + \varphi(V, x_2)$$

where φ is a function depending only on temperature.

The function φ is the greater, the bigger is the difference $p_1^\circ - p_2^\circ$. The change in the sign of $\varphi(V, x_2)$ coincides with that of $p_1^\circ - p_2^\circ$. We may therefore assume that these quantities are proportional to each other, and thus the preceding equation becomes

$$p = p_1^\circ x_1 + p_2^\circ x_2 + a x_1 x_2 (p_1^\circ - p_2^\circ) \quad (6.28)$$

where p_1° and p_2° = pressures of the pure components at molar volumes equal to that of the gas mixture

a = constant characteristic of a given mixture.

Equation (6.28) was generalized by I. Krichevsky and V. Markov (1940) for a ternary mixture:

$$p = p_1^\circ x_1 + p_2^\circ x_2 + p_3^\circ x_3 + a_{1,2}x_1x_2(p_1^\circ - p_2^\circ) + \\ + a_{2,3}x_2x_3(p_2^\circ - p_3^\circ) + a_{1,3}x_1x_3(p_1^\circ - p_3^\circ) \qquad (6.29)$$

where $a_{1,2}$, $a_{2,3}$ and $a_{1,3}$ are the constants of the equations for the corresponding binary mixtures.

The Krichevsky-Kazarnovsky equation is distinguished by its high accuracy for both low and high pressures (the mean error of calculations is about 0.5%). Calculations with its aid require few data and are considerably simplified if the mixture contains no polar components, since in this case the constant a does not depend on the temperature.*

Table 7 illustrates the relative accuracy of some of the equations considered above for a number of gas mixtures.

Table 7. **Comparative Accuracy of Selected Equations of State for Mixtures (Maximum and Average Errors in Per Cent)**

Equation	Ar-C_2H_4 $t = 25$ °C $p = 1$-125 atm		N_2-H_2 $t = 0$-300 °C $p = 1$-1000 atm		H_2-CO_2 $t = 0$-200 °C $p = 50$-500 atm		N_2-CO_2 $t = 0$-200 °C $p = 50$-500 atm	
	max.	av.	max.	av.	max.	av.	max.	av.
(6.14)	9.0	3.0	24.0	—	—	—	—	—
(6.16)	31.5	16.0	1.66	0.45	15.0	5.4	—	—
(6.25)	—	—	9.0	3.4	—	—	—	—
(6.27)	10.6	6.0	7.87	1.16	19.5	6.5	9.4	2.15
(6.28)	1.62	0.40	2.06	0.65	2.2	0.80	2.6	1.18

Example 9. Use Eq. (6.25) to calculate the pressure of one mole of the mixture H_2 + CO (2 : 1) if its density at $t = 25$ °C is 0.011 66.

Solution. Using the data of Table 6, we calculate the coefficients with the aid of Eqs. (6.26):

$$\sqrt[3]{(A_0)_m} = 0.667\sqrt[3]{0.124\,04} + 0.333\sqrt[3]{1.3445} = 0.621$$

$$a_m = 0.667 \times 0.056\,18 + 0.333 \times 0.026\,17 = 0.046\,18$$

$$(B_0)_m = 0.667 \times 0.020\,22 + 0.333 \times 0.050\,46 = 0.0303$$

$$b_m = 0.667 \times (-0.007\,22) + 0.333 \times (-0.006\,91) = -0.007\,117$$

$$c_m = 0.667 \times 20\,000 + 0.333 \times 420\,000 = 153\,200$$

* A. Rozen (1941) and M. Temkin (1943) showed that the Krichevsky-Kazarnovsky equation can be derived on the basis of a theoretically substantiated equation of state with the second virial coefficient (see p. 150); Temkin also showed that the constant a, generally speaking, depends on temperature.

Next by Eq. (6.25) we find

$$p = \frac{0.082\,06 \times 298.2}{0.085\,76^2}\left(1 - \frac{153\,200}{0.085\,76 \times 298.2^3}\right)\times$$

$$\times\left[0.085\,76 + 0.0303\left(1 - \frac{-0.007\,117}{0.085\,76}\right)\right] -$$

$$- \frac{0.621}{0.085\,76^2}\left(1 - \frac{0.046\,18}{0.085\,76}\right) = 344.6$$

which differs from the experimentally found value (350 atm) by 1.5%. Calculations by Eq. (6.13) would have given a discrepancy of 18.5%.

Example 10. Below are given the pressures of hydrogen, nitrogen and a nitrogen-hydrogen mixture (1 : 3) at equal densities calculated according to the corresponding compressibilities:

p	0.001 00	0.001 00	0.001 80	0.001 80
t	−50	−100	0	100
$p^\circ_{H_2}$.	214	367	567	782
$p^\circ_{N_2}$.	170	377	631	1013
p	207	369	578	818

Find Eq. (6.28) for a nitrogen-hydrogen mixture and calculate the mean error for the indicated conditions, comparing the results of calculations with calculations by Eq. (6.27).

Solution. Using the given values of the pressures, we calculate the values of $\varphi(V, x_2)$ in Eq. (6.28), and plot the quotients obtained

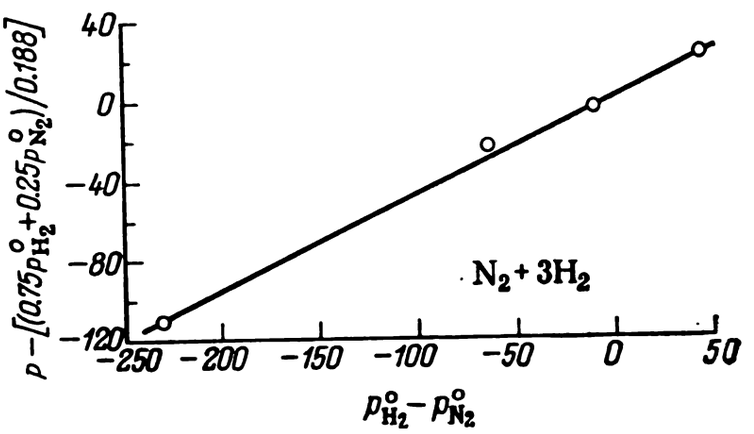

Fig. 27. Compressibility of gas mixtures.
Checking of Eq. (6.28). (See Example 10)

by dividing these values by the product of the mole fractions of the mixture components versus the pressure difference $p^\circ_{H_2} - p^\circ_{N_2}$ (Fig. 27). We draw a straight line through the obtained points

(and through the origin of coordinates) whose slope (0.47) equals the constant of Eq. (6.28). Thus we get the equation

$$p = p^\circ_{H_2} x_{H_2} + p^\circ_{N_2} x_{N_2} + 0.47 x_{H_2} x_{N_2} (p^\circ_{H_2} - p^\circ_{N_2})$$

which holds for nitrogen-hydrogen mixtures having any composition. The average error of the calculations is less than 0.2%. Calculations by Eq. (6.27) give an average error of 1.4%.

6.3. FUGACITY

The practical use of equations of state is quite difficult and time consuming. For instance, the change in the Gibbs energy in an isothermal process in accordance with Eq. (5.25) will equal $\int_1^2 V\,dp$. But to find this integral it is necessary to insert into the integrand the dependence of V on p (or p on V). For an ideal gas, this problem is solved very simply in accordance with the Mendeleev-Clapeyron equation

$$\Delta G_T = RT \ln \frac{p_2}{p_1} \tag{6.30}$$

Matters are different with a real gas, for which it is impossible to take the integral $\int V\,dp$ in the general case, i.e. for any values of p and T.

G. Lewis (1901) proposed a different procedure to simplify the calculations. He introduced a certain function f of p called the **fugacity**, whose use instead of the pressure in Eq. (6.30) makes it possible to apply the latter to a real gas.

Although formal, this procedure nevertheless solves the problem. In replacing pressure with fugacity, we retain the simple mathematical form of the thermodynamic relationships for an ideal gas.

Thus, the new function is determined by the equation

$$\left.\begin{aligned} &\Delta G_T = RT \ln \frac{f_2}{f_1} \quad \text{or} \quad dG_T = RT\,d \ln f \\ &\text{or} \\ &G = RT \ln f + \varphi(T) \quad \text{or} \quad f = \varphi(T) \exp\left(\frac{G}{RT}\right) \end{aligned}\right\} \tag{6.31}$$

Consequently, in accordance with Eq. (5.25) we have

$$\left(\frac{\partial \ln f}{\partial p}\right)_T = \frac{V}{RT} \tag{6.32}$$

whence

$$RT \ln \frac{f_2}{f_1} = \int_1^2 V \, dp \tag{6.33}$$

It follows from Eq. (6.32) that the values of f at high pressures (and low temperatures) greatly differ from p. Thus, at $t = 0\,°C$ and $p = 1200$ atm, we have $f_{CO} = 2663$ atm, at $t = 0\,°C$ and $p = 1000$ atm we have $f_{NH_3} = 204$, and for N_2 at $t = -75\,°C$ and $p = 6000$ atm we have $f \approx 2 \times 10^6$ atm, i.e. fugacity becomes incompatible with pressure.

Fugacity can be defined as the pressure a given real system must produce to have the same action as an ideal system. Thus, it can be called the corrected (effective) pressure. It characterizes the deviation from the ideal state and, like the pressure for an ideal gas, can be considered as a measure of the dispersibility of a substance, i.e. of the tendency of the latter to occupy a greater volume. When a real gas approaches the ideal state, the fugacity approaches the pressure in value, so that for an ideal gas at all pressures both quantities become equal,* i.e.

$$\lim_{p \to 0} \frac{f}{p} = 1$$

Hence it follows that the dimension of f coincides with that of p.

It should be stressed that the substitution of f for p in the equations of an ideal gas when passing over to a real gas holds only for an isothermal process, since according to Eq. (6.31) fugacity is a specific *isothermal* function.

To characterize the degree of deviation of a gas from the ideal state, the quantity

$$\gamma = \frac{f}{p} \tag{6.34}$$

is also introduced. It is called the **activity coefficient** or the **fugacity coefficient**.

6.3.1. Standard State

Gases. Since the absolute value of the Gibbs energy is unknown, we also cannot determine the absolute value of f (except for an ideal gas, for which $f = p$). It is therefore necessary first to introduce a

* This condition is obligatory, since from a comparison of the equations $dG = RT\, d \ln p$ and $dG = RT\, d \ln f$ it only follows that for an ideal gas f is *proportional* to p.

certain standard state which must serve as the beginning of counting of this function. It would be possible to select the state of a gas at the infinitely low pressure p^*, when $f^* = p^*$, but this is not convenient because Eq. (6.31) will include the quantity $\ln p^* = -\infty$.

By the standard state of a pure gas at each temperature is meant the hypothetic state of an ideal gas whose fugacity at this temperature equals unity, and whose enthalpy equals that of the real gas at the same temperature and at a pressure equal to zero. The notion of the standard state of a gas can be illustrated by the following mental experiment (Fig. 28) : let us first isothermally expand a real gas which is in an arbitrary state (point *a*) to an infinitely low pressure p^* (see also Fig. 7, p. 49), and then compress it along an isotherm of an ideal gas to $p = 1$. Now its state will correspond to point *O* at which $f = p = 1$.

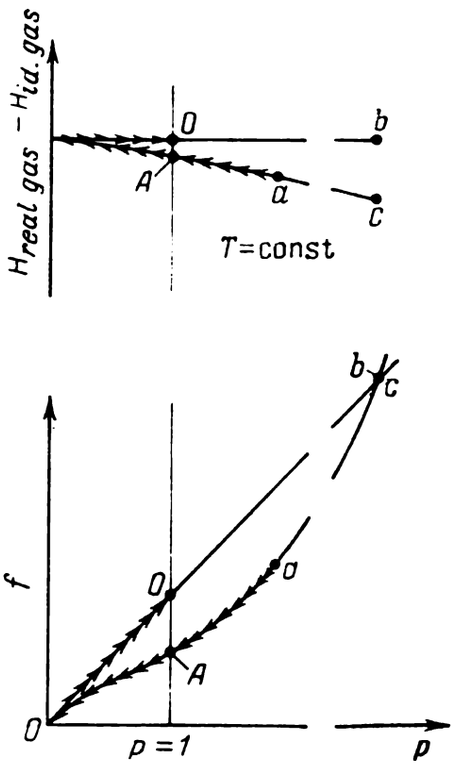

Fig. 28. Illustrating the definition of the standard state of a gas

A comparison of the upper drawing with the lower one shows that if at a certain (high) pressure the isotherms of the real and ideal gases intersect, i.e. $f = p$ (combined points *b* and *c*), this does not mean that both gases are in an identical thermodynamic state (at this point the Gibbs energies of the real and ideal gases are equal, but the enthalpies are different).

Although the standard state cannot correspond to the real state of a substance, for ordinary conditions ($p = 1$ atm) we can consider that the state of a gas is virtually the same as the standard state. For an ideal gas regardless of the temperature, we have $f = p$, and at all temperatures $f^\circ = 1$ atm.

The ratio between f for a given state and f° at the same temperature is called the **activity** and is denoted by the symbol a. Hence

$$G - G^\circ = RT \ln \frac{f}{f^\circ} = RT \ln a \qquad (6.35)$$

Since $f^\circ = 1$ atm for gases, then $a = f$ for them.

The introduction of the standard state permits us to find the value of f for any pressure with the aid of the equation

$$G - G^\circ = RT \ln f \qquad (6.36)$$

Pure Liquids and Solids. The standard state of a pure **condensed phase** is the state of the pure substance which at the *given* temperature is under a pressure of 1 atm. If at $p = 1$ atm for gases we have $f = 1$ for all temperatures, for a liquid (or a crystalline body) this equality is observed only at one temperature, since the condensed phase is in equilibrium with its saturated vapour whose pressure changes with the temperature. Consequently, for a liquid or crystalline body in general, we have $a \neq f$. For this reason, *the real state of a liquid (crystalline substance) under a pressure of 1 atm is taken as the standard state at each temperature.*

Because the molar Gibbs energies are equal in phases coexisting in equilibrium, in accordance with Eq. (6.31) the fugacity of a pure condensed phase equals that of its saturated vapour. Hence, when several phases coexist at the same temperature, the tendency of a substance to leave each phase will be the same. If equilibrium is absent, the substance will pass from the phase where this tendency manifests itself more to the other one. We thus have an analogy between f characterizing physical processes (or p characterizing them in the ideal case) and, for example, T characterizing the intensity and direction of heat exchange.

Since f of a liquid (solid) equals f of its saturated vapour, it is possible to determine the properties of a liquid (solid) by expressing them through the properties of its saturated vapour.

The influence of p on f of a condensed phase is determined by Eq. (6.32); considering $V = \text{const}$, we get

$$\ln \frac{f_2}{f_1} = \frac{V(p_2 - p_1)}{RT} \tag{6.37}$$

or by Eq. (6.35)

$$\ln a = \frac{V(p - 1)}{RT} \tag{6.38}$$

Equation (6.37) can also be used to calculate the change in f of a liquid when the external pressure changes from that of the saturated vapour over the liquid to a certain high pressure p_{ext}. In this case in Eq. (6.37) T is the boiling point, p is the saturated vapour pressure, f_1 is the fugacity of the liquid equal to that of its vapour in equilibrium with it, and f_2 is the fugacity of the liquid at the high pressure.

6.3.2. Temperature Dependence of Fugacity

Differentiation of the equation $G^* - G = RT \ln (f^*/f)$ with respect to the temperature yields

$$\left[\frac{\partial(G^* - G)}{\partial T}\right]_p = R \ln \frac{f^*}{f} - RT\left(\frac{\partial \ln f}{\partial T}\right)_p$$

From these two equations, we find

$$\left[\frac{\partial(G^* - G)}{\partial T}\right]_p = \frac{G^* - G}{T} - RT\left(\frac{\partial \ln f}{\partial T}\right)_p$$

Since from Eq. (5.26) it follows that $(\partial \Delta G/\partial T)_p = \Delta G/T - \Delta H/T$, we get

$$\left(\frac{\partial \ln f}{\partial T}\right)_p = \frac{H^\circ - H}{RT^2} \tag{6.39}$$

where the quantity $H^\circ - H$ equals the change in the enthalpy upon isothermal expansion from the given pressure to an infinitely small one ($H \neq H^\circ$).

Assuming that $H^\circ - H$ does not depend on T (this is true only for a comparatively small temperature interval), we get the equation

$$\ln \frac{f_2}{f_1} = \frac{H^\circ - H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{6.40}$$

6.3.3. Methods of Calculating Fugacity

Graphical Methods. We shall consider two graphical methods of calculating fugacity.

1. We introduce the quantity

$$\alpha = \frac{RT}{p} - V \tag{6.41}$$

called the volume correction for a real gas and characterizing the degree of deviation of a real gas from an ideal gas. Hence in accordance with Eq. (6.32), we have

$$RT \ln \frac{f}{f'} = RT \ln \frac{p}{p'} - \int_{p'}^{p} \alpha \, dp$$

Mentally displacing the isobar p' to the region of infinitely large volumes V_∞, where $p' = p^* = f^*$, after cancelling and discarding the superscript $'$, we get

$$RT \ln f = RT \ln p - \int_{p^*}^{p} \alpha \, dp$$

Since we can consider p^* equal to zero, this equation becomes

$$RT \ln f = RT \ln p - \int_{0}^{p} \alpha \, dp \tag{6.42}$$

To determine f on the basis of experimental data, the value of α is calculated for each value of V (at the corresponding value of p), and then α is plotted against p (Fig. 29). For $p = 0$, the value of α is determined by extrapolation, which may be done with sufficient

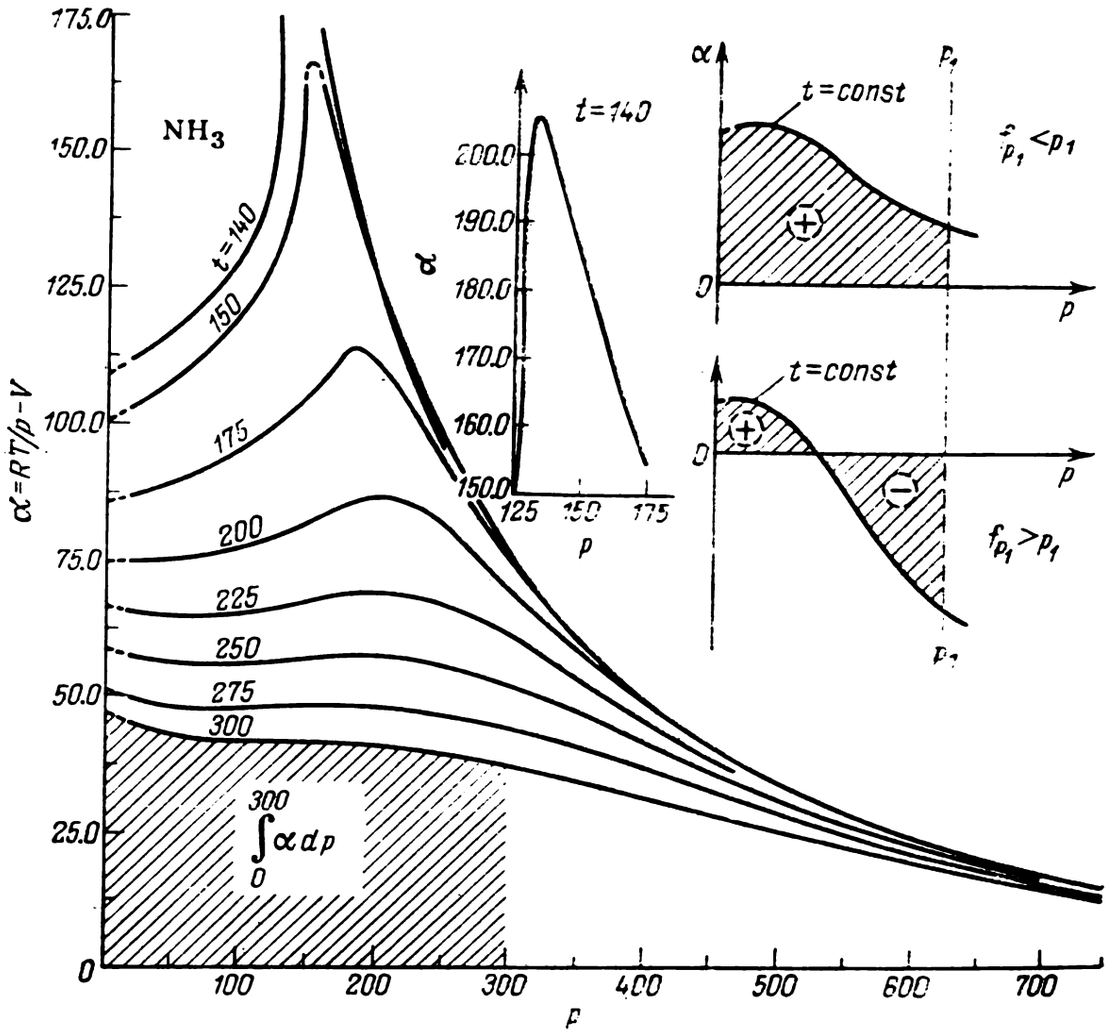

Fig. 29. Pressure dependence of $\alpha = \dfrac{RT}{p} - V$.

Showing the graphical calculation of fugacity

accuracy along a straight line, since experimental data show that $\alpha \to$ const when $p \to 0$.* After plotting the graph, the second term of the right-hand side of Eq. (6.42) is found by graphical integration.

The relationship between the contribution of f and p is determined by the shaded area in Fig. 29. Hence, we have $f = p$ not only at $p = 0$, but also at high pressures, when the corresponding area equals zero. This does not mean, of course, that the gas becomes ideal at

* This does not contradict the fact that at $p \to 0$ the properties of a gas are described by Eq. (6.7), since it follows from Eq. (6.41) that at $p \to 0$ we have $pV = RT$, even if $\alpha \neq 0$.

a high pressure. Indeed, if the gas were ideal in these conditions, the change in p along an isotherm could not violate the equality $f = p$. At the same time, an insignificant change in the pressure in either direction is sufficient for the equality to be violated (see Fig. 28 and Fig. 40, p. 192). This can also be confirmed by analysing Fig. 31 (p. 171).

2. We write down Eq. (6.42) in the form

$$RT \ln f = RT \ln p - W^* \tag{6.43}$$

where $W^* = \int_{p^*}^{p} (V_i - V)dp$ on the plot of p versus V equals the area limited by the isotherms of the ideal and real gases and the isobar corresponding to the pressure for which f is being calculated (see Fig. 7, p. 49). It follows from Eq. (6.42) that $f < p$ at $W^* > 0$. If $W^* < 0$, then $f > p$. This indicates that the isotherms of the ideal and real gases have changed places on the $p = V$ graph, beginning from the point of intersection of the isotherms (in the direction of high pressures), the value of the area is negative. Finally, if $W^* = 0$, then $f = p$.

The first method of calculating f is more dependable than the second, since (1) the area being calculated is limited by only one curve; (2) extrapolation of the curve to the value $p = 0$ is almost exact; and (3) at the same value of the graduations the area is much greater.

One might wonder why it was necessary to introduce the standard state when the formulas for the calculations were found without even mentioning it. It is not difficult to show, however, that the value of f in Eq. (6.42) is counted from the quantity f°. Indeed, the introduction of the concept of the "standard state" was connected with two hypothetical processes (see Figs. 7 and 28): (1) a real gas (point a) expands from the pressure p to an infinitely small pressure p^*; and (2) the gas from this infinitely small pressure is compressed along an isotherm of an ideal gas to $p = 1$.

These processes are connected with a change in the Gibbs energy

$$\int_{p}^{p^*} V\,dp + \int_{p^*}^{1} V_i\,dp = RT \ln \frac{p^*}{f} + RT \ln \frac{1}{p^*} = -RT \ln f$$

whence

$$RT \ln f = \int_{p^*}^{p} V\,dp - \int_{p^*}^{1} V_i\,dp$$

since

$$\int_{p^*}^{p} V\,dp = \int_{p^*}^{p} V_1\,dp - W^*$$

then

$$RT\ln f = \int_{p^*}^{p} RT\,d\ln p - W^* - \int_{p^*}^{p} RT\,d\ln p =$$

$$= RT\ln p - W^* = RT\ln p - \int_{p^*}^{p} \alpha\,dp$$

Analytical Methods. The calculations are based on finding the integral (6.33) for a real gas with the aid of an equation of state.

Thus, if it is necessary to find f at a comparatively low pressure, we can use Eq. (6.19). It is a cubic equation with respect to V, therefore it is simpler to integrate by expressing p as a function of V. Taking a definite integral of $V\,dp$ and then resorting to the same procedure as when deriving Eq. (6.42), we obtain *

$$\ln f = \ln \frac{RT}{V-b} + \frac{b}{V-b} - \frac{2a}{RTV} \tag{6.44}$$

---

* Indeed, from Eq. (6.19) it follows that

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

whence

$$dp = \frac{-RT\,dV}{(V-b)^2} + \frac{2a\,dV}{V^3}$$

Hence Eq. (6.33) acquires the form

$$RT\ln\frac{f}{f'} = \int_{p'}^{p} V\,dp = -RT\int_{V'}^{V}\frac{V\,dV}{(V-b)^2} + 2a\int_{V'}^{V}\frac{dV}{V^2} =$$

$$= -RT\left[\int_{V'}^{V}\frac{(V-b)\,dV}{(V-b)^2} + b\int_{V'}^{V}\frac{dV}{(V-b)^2}\right] +$$

To find f, we must know not only the constants of Eq. (6.19), but also the value of the volume of the real gas. It is wrong to substitute the value of V from Eq. (6.7) for the latter; although it is somewhat flawed, the volume from Eq. (6.19) is often substituted in practical calculations.

For moderate pressures, the equation

$$\ln f = \ln p + \frac{9T_{cr}}{128p_{cr}T}\left(1 - 6\frac{T_{cr}^2}{T^2}\right)p \tag{6.45}$$

is used, where f is expressed through Eq. (6.20). For higher pressures, the equation

$$\ln f = \ln RT - \ln V + \frac{1}{RTV}\left(2\beta + \frac{3\gamma}{2V} + \frac{4\delta}{3V^2}\right) \tag{6.46}$$

which is obtained from Eq. (6.22), can be used.

These equations are derived similarly to Eq. (6.44).

An *approximate method of calculating f* is based on the assumption that in the region of low pressures $\alpha \approx$ const (see Fig. 29). Hence Eq. (6.42) becomes

$$RT \ln f = RT \ln p - \alpha p \quad \text{or} \quad \frac{f}{p} = \exp\left(-\frac{\alpha p}{RT}\right)$$

$$+ 2a\int_{V'}^{V} \frac{dV}{V^2} = -RT\left|\ln(V-b) - \frac{b}{V-b}\right|_{V'}^{V} - 2a\left|\frac{1}{V}\right|_{V'}^{V}$$

i.e.

$$RT \ln \frac{f}{f'} = RT\left[-\ln(V-b) + \ln(V'-b) + \frac{b}{V-b} - \frac{b}{V'-b}\right] - \frac{2a}{V} + \frac{2a}{V'}$$

Cancelling RT in both parts of the equation and substituting V_∞ for V', i.e. resorting to the same procedure which we used in deriving Eq. (6.42), we get

$$\ln \frac{f}{f^*} = -\ln(V-b) + \ln V_\infty + \frac{b}{V-b} - \frac{2a}{RTV}$$

But since $f^* = p^* = RT/V_\infty$, the preceding equation becomes

$$\ln f - \ln f^* = -\ln(V-b) + \ln RT - \ln p^* + \frac{b}{V-b} - \frac{2a}{RTV}$$

from which after transformations we get Eq. (6.44).

and for small values of $x = \alpha p/RT$, when after expansion of e^{-x} into a series * we may limit ourselves to only the first two terms, we have

$$\frac{f}{p} = 1 - \frac{\alpha p}{RT}$$

or by Eqs. (6.7) and (6.41)

$$f = \frac{p^2}{RT/V} = \frac{p^2}{p_i} \quad \text{or} \quad p = \sqrt{f p_i} \tag{6.47}$$

In other words, the actual pressure is the geometric mean of the fugacity and the pressure calculated for an ideal gas.

Apart from its simplicity, the approximate equation (6.47) is convenient because the p-V-T-data along the entire length of the isotherm up to the given pressure p are not needed.

6.4. THROTTLING

The experiment involving the expansion of a gas described at the beginning of Sec. 6.1 was not sufficiently accurate, since as a result of the low heat capacity of the gas in comparison with that of the vessels and the calorimeter, a small change in temperature could not be detected (calculations showed that in the conditions of this experiment $\Delta t = -0.0045$ K). This is why new experiments were run. The gas was passed along a wooden tube through a plug of cotton with a sufficiently high resistance to ensure a constant pressure to the left and the right from it (see the diagram in Fig. 30 **). The slow motion of the gas being forced through the porous partition also made it possible to ignore the change in its kinetic energy. The experiment proceeded adiabatically and was attended by a loss of pressure. The work of the process equalled

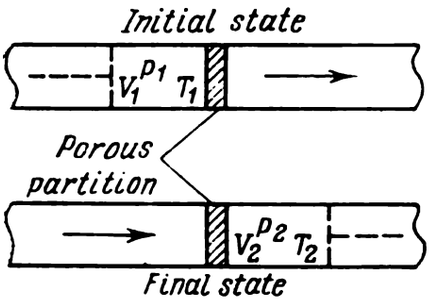

Fig. 30. Diagram of experiment involving the throttling of a gas

$$W = p_1(0 - V_1) + p_2(V_2 - 0) = \\ = -p_1V_1 + p_2V_2$$

(If the gas were ideal, then $T = \text{const}$ and by Eq. (6.5) we would have $p_1 = p_2$, i.e. $W = 0$.) But since $Q = 0$, then $-\Delta U = W$, i.e.

$$U_1 + p_1V_1 = U_2 + p_2V_2 \quad \text{or} \quad H_1 = H_2 \tag{6.48}$$

* $e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \ldots$.

** We consider that the pressure is conditionally applied to imaginary pistons separating a certain amount of the gas (for example one mole).

The ratio of the change in the temperature of a gas as a result of throttling, i.e. non-equilibrium expansion at a sharp increase in the resistance, to the change in the pressure is called the **throttling effect** or the **Joule-Thomson effect.**

The **Joule-Thomson coefficient** is determined by the expression

$$\mu_J \equiv \left(\frac{\partial T}{\partial p}\right)_H \tag{6.49}$$

In practice it is usually defined as the change in temperature corresponding to a pressure drop of 1 atm in throttling.

Equation (6.48) and the subscript "H" in expression (6.49) should not be understood as a condition of constant enthalpy. In a throttling *process*, the enthalpy changes, since in the constricted section (in practice — in the throttling valve, at the place of installation of a gate valve on a pipe, etc.) eddies appear that cause an increase in the kinetic energy of the stream, which with the adiabatic nature of the process results in diminishing of the enthalpy. Only after the gas has passed the local resistance does the enthalpy acquire its original value (if we ignore the difference in kinetic energies at both sides of the resistance). Consequently, although for determining the properties of a substance after throttling, a line $H = \text{const}$ is drawn on the H-S diagram, this is only a graphical procedure which permits us to find all the properties of a substance after throttling according to the values of its properties before throttling (for instance according to p_1 and T_1) and a property after throttling (for instance according to the counterpressure p_2).

The indeterminacy of the values of H between points *1* and *2* cannot affect the results of the calculations, since they depend on the properties of the system in the initial and final states, and not on the path followed by the process.

In accordance with Eq. (1.8), written down for the functional relationship $\varphi(H, p, T) = 0$, expression (6.49) will become

$$\mu_J = \frac{-(\partial H/\partial p)_T}{(\partial H/\partial T)_p}$$

or in accordance with Eqs. (3.10) and (4.23)

$$\mu_J = \frac{T(\partial V/\partial T)_p - V}{C_p} \tag{6.50}$$

Equation (6.50) can be used not only for gases, since an experiment involving throttling can also be conducted with a liquid.

In practice, we most often work with the **integral throttling effect,** i.e. with a change in temperature

$$T_2 - T_1 = \int_{p_1}^{p_2} \mu_J \, dp \tag{6.51}$$

corresponding to a finite lowering of the pressure in a non-equilibrium adiabatic process.

The change in temperature in throttling can be found by thermodynamic diagrams (in particular H-S diagrams) * and by an equation of state (or according to experimental p-V-T-data). Thus, if for moderate pressures we use Eq. (6.19), after simplification we get

$$\frac{\Delta T}{\Delta p} \approx \frac{2a/RT - b}{C_p} \tag{6.52}$$

The sign of the Joule-Thomson coefficient μ_J (positive in cooling and negative in heating, since $p_2 < p_1$) depends on the nature of the gas and on the conditions of throttling, i.e. on p and to a greater extent on T.

Let us consider in greater detail the magnitude and sign of the Joule-Thomson coefficient. Combining Eqs. (4.23), (6.50) and (2.10), we obtain

$$\mu_J C_p = -\left(\frac{\partial U}{\partial p}\right)_T - \left[\frac{\partial (pV)}{\partial p}\right]_T$$

or

$$\mu_J C_p = -\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T - \left[\frac{\partial (pV)}{\partial p}\right]_T \tag{6.53}$$

The internal pressure $(\partial U/\partial V)_T$ is a positive quantity, while the derivative $(\partial V/\partial p)_T$ is negative. Therefore, the first term in the right-hand side of Eq. (6.53) is negative. The quantity $[\partial(pV)/\partial p]_T$ for all gases at ordinary temperatures and not very high pressures is negative (according to the condition that $p_2 < p_1$); at high pressures it is positive, since the isotherms $pV = \varphi(p)$ pass through a minimum (Fig. 31). Hydrogen and helium are an exception (they will be discussed below).

Thus, for all gases at ordinary temperatures and moderate pressures we have $\mu_J > 0$, i.e. throttling is attended by cooling. With a growth in the pressure, the second term of the right-hand side of Eq. (6.53) diminishes and then becomes positive (see Fig. 31); the first term may be considered independent of the pressure, since $(\partial U/\partial V)_T$ increases with a growth in the pressure **, while $(\partial V/\partial p)_T$

* See, for example, the author's supplement "The Entropy-Enthalpy Diagram" to the Russian translation of [A10] [Dodge, B. F. *Khimicheskaya termodinamika v primenenii k khimicheskim protsessam i khimicheskoi tekhnologii.* Moscow, Izdatinlit (1950)].

** This conclusion can also be derived from the approximate relationship

$$\left(\frac{\partial U}{\partial V}\right)_T \approx \frac{a}{V^2}$$

which follows from Eq. (6.19).

diminishes. With a growth in the pressure, this causes μ_J to diminish and then pass through zero (the **inversion point**). When the second term of the right-hand side of Eq. (6.53) becomes greater than the first in absolute value, μ_J acquires a negative value, i.e. the gas

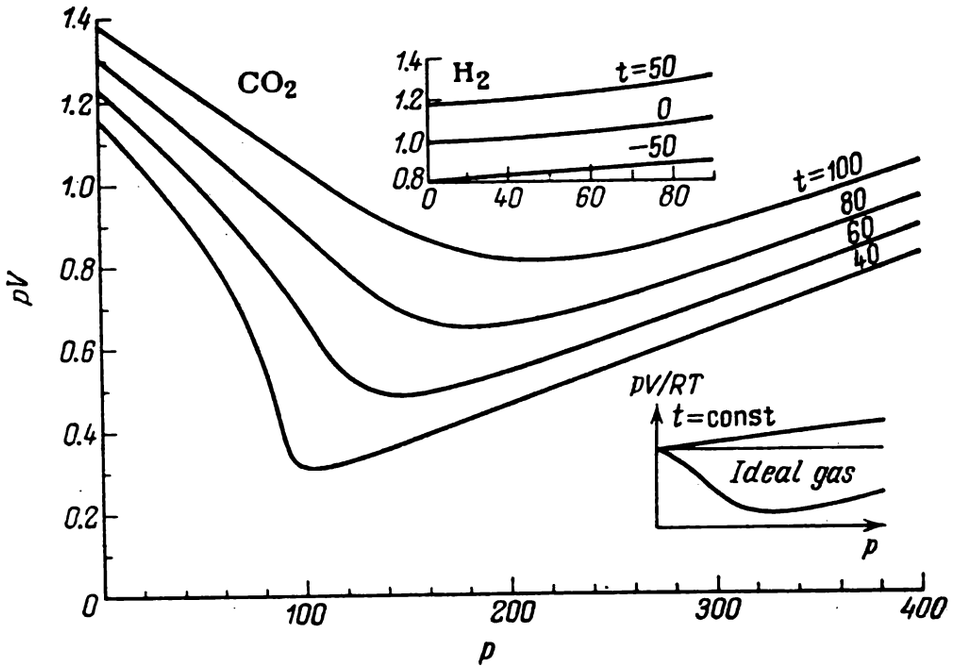

Fig. 31. Pressure dependence of product pV (related to p in standard conditions) for carbon dioxide and hydrogen

becomes heated. The heating will be the more considerable, the higher is the initial pressure.

With lower temperatures, the isotherms $pV = \varphi(p)$ become displaced downward, and both of their branches become steeper, the minimum shifting toward low pressures. From this it follows that, first, at low pressures the numerical value of the second term of the right-hand side of Eq. (6.53) will grow with decreasing temperature, i.e. the cooling effect will grow, and, second, the inversion points will be displaced in the direction of high pressures, i.e. the inversion temperature will diminish with increasing pressure.

At elevated temperatures, throttling is attended by heating, since the minimum on the isotherms $pV = \varphi(p)$ vanishes, i.e. at any pressures we have $p_2V_2 < p_1V_1$.

Since in practice throttling, as a rule, occurs at not very high pressures and temperatures, all gases (except for H_2 and He) cool, which upon their repeated throttling (and cooling) causes condensation. The throttling of hydrogen and helium, whose isotherms $pV = \varphi(p)$ for ordinary and high temperatures and for any pressures continuously ascend (see Fig. 31), i.e. $[\partial(pV)/\partial p]_T > 0$, is accompanied by heating ($\mu_J < 0$) (this is why hydrogen ignites when it flows out of damaged pipes). For sufficiently low temperatures,

their isotherms $pV = \varphi(p)$ are similar to those for other gases at ordinary temperatures. Consequently, with lowering of temperature, μ_J, after passing through zero, becomes positive, i.e. H_2 and He behave in the same way as all other gases at ordinary temperatures. It follows that hydrogen and helium, whose inversion temperature is quite low, must be cooled quite considerably before throttling to be liquefied. In practice, this cooling is achieved with the aid of liquid air (for hydrogen) and liquid hydrogen (for helium).

The problem of the nature of the change in the temperature in throttling can also be solved by analysing an equation of state of a real gas. Let us consider Eq. (6.19) as an example. For simplicity, we can analyse two limiting cases: (1) the volume of the molecules is negligibly small, and the forces of cohesion are great; and (2) the volume of the molecules is great, and the forces of cohesion are small.

Ignoring in the first case (low temperatures) the constant b in Eq. (6.19), we get $p_2V_2 - p_1V_1 = R(T_2 - T_1) - a(1/V_2 - 1/V_1)$. The quantity $p_2V_2 - p_1V_1$ is positive (although $T_2 < T_1$, but $V_2 \gg V_1$), i.e. the work of pushing back the gas at the right-hand side of the resistance is greater than that of pushing the gas through the resistance. This results in cooling: the difference $p_2V_2 - p_1V_1$ is replenished by a reduction in the internal energy. In addition, the cohesive energy grows (the potential energy due to the forces of interaction), i.e. the energy of thermal motion is used both for doing work and for increasing the cohesive energy.

In the second case, we may disregard the quantity a in Eq. (6.19). Therefore, $p_2V_2 - p_1V_1 = R(T_2 - T_1) + b(p_2 - p_1)$; the quantity $p_2V_2 - p_1V_1$ will be negative ($T_2 > T_1$, but $p_2 \gg p_1$). The surplus work will go to increase the internal energy, which causes an increase in the energy of thermal motion, i.e. heating of the gas.

It is easy to see that if p_1V_1 is equal to and even somewhat greater than p_2V_2, then in throttling cooling will occur because of the decrease in the energy of thermal motion, since in these cases the increase in the internal energy may be less than the increase in the energy of interaction.

Thus, the constants a and b of Eq. (6.19) reflect opposite action [this also directly follows from Eq. (6.52)] — if a is great and b is small, then $\mu_J > 0$; conversely, if b is great and a is small, then $\mu_J < 0$. Real cases are somewhere in-between these two. Therefore, both effects are often superimposed, their values changing for different gases and for different pressures and temperatures, and it is exactly this circumstance that causes the sign of μ_J to change.

The sign of μ_J follows from that of the numerator of Eq. (6.50). If we have $T(\partial V/\partial T)_p > V$, then the gas is cooled; the condition

of heating is the inequality $T(\partial V/\partial T)_p < V$; finally, when $T(\partial V/\partial T)_p = V$, inversion sets in.*

The condition of inversion can also be obtained from Eq. (6.52), which in combination with the condition $\mu_J = 0$ gives

$$T_{inv} \approx \frac{2a}{Rb} \tag{6.54}$$

It follows from Eqs. (6.54) and (6.52) that when $T \gtrless T_{inv}$, heating occurs ($T_2 > T_1$). Conversely, when $T < T_{inv}$, cooling occurs ($T_2 < T_1$).

Since μ_J depends on T and p (the influence of the pressure is especially appreciable when its value is high), the inversion points will be displaced in p-V coordinates, forming an **inversion curve**. A graph of T against V (Fig. 32) can be used to find it in accordance with Eq. (6.50). Tangents to the isobars intersect the axis of abscissas at points that are at a distance of $T(\partial V/\partial T)_p - V$ from the origin of coordinates. If these points are to the left of the origin of coordinates, the gas will cool upon throttling, and if they are to the right, it will be heated.

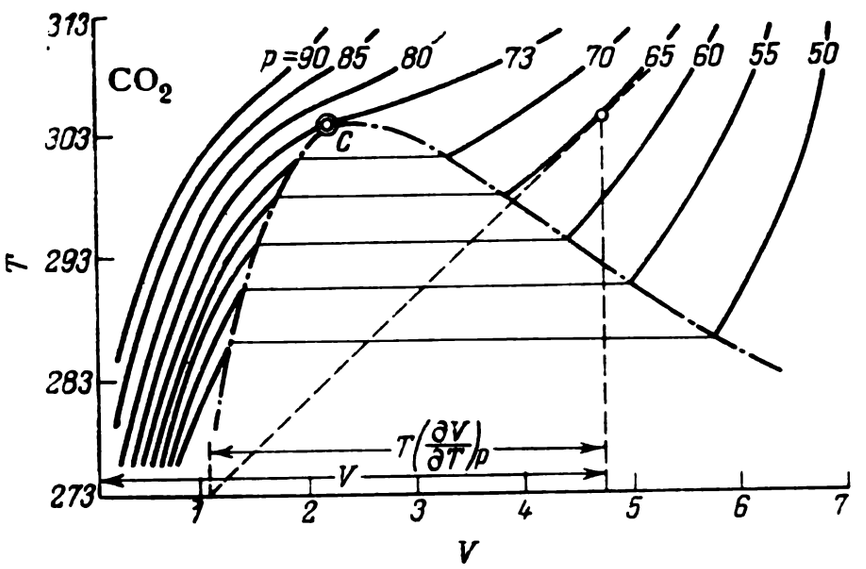

Fig. 32. Illustrating the method of graphical determination of the Joule-Thomson coefficient (C is the critical point)

Examination of Fig. 32 shows that each isobar has a point at which a tangent to the curve will pass through the origin of coordinates. There are such points both on the section of the isobar corre-

* Here the following remark is appropriate: if for an ideal gas $\mu_J = 0$ [this follows, for instance, from Eq. (6.50)], the reverse conclusion is not true, since the condition $\mu_J = 0$ precisely characterizes a *real gas* at the points of inversion (these points obviously coincide with the ones at which $f = p$). It should be noted in passing that for any gas for which the isobars are straight lines we have $\mu_J = 0$; this follows from Eq. (6.50).

sponding to the gaseous phase and on the section corresponding to the liquid phase. After finding on each curve the pair of points satisfying the condition $\mu_J = 0$, we can plot an inversion curve (Fig. 33).

An analysis of Figs. 32 and 33 also permits us to determine the nature of the change in the temperature in throttling. A glance at Fig. 32, for example, shows that μ_J at the same pressure is the greater (and cooling is the more intense), the lower is the temperature, i.e. movement along any isobar downward indicates a reduction in V and an increase in $T(\partial V/\partial T)_p$. It follows from the same figure that at elevated temperatures $V > T(\partial V/\partial T)_p$; consequently, in these conditions heating will occur. Heating also occurs at very high pressures (at any temperature). Hence, the region in Fig. 33 outside of the inversion curve corresponds to heating in throttling; conversely, the region under this curve corresponds to cooling.

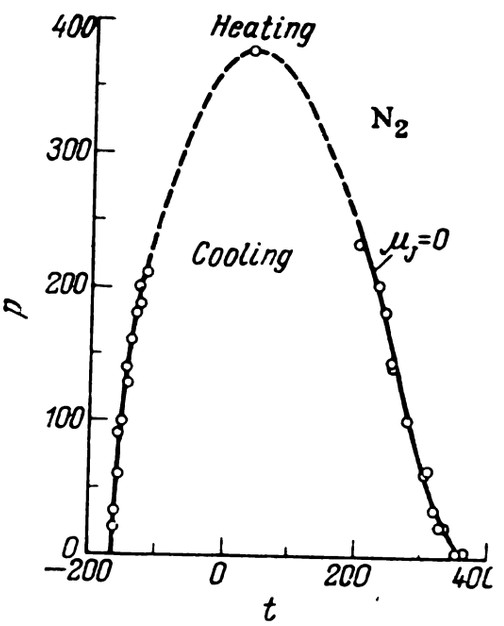

Fig. 33. Inversion curve

Throttling can be conducted not only adiabatically, but also isothermally *. Here in the case of a cooling effect, heat must be supplied to the system (for example from a heat exchanger installed after the throttle valve) equal to the change in enthalpy. Combining Eqs. (3.11) and (6.50), we get

$$\left(\frac{\partial H}{\partial p}\right)_T = -\mu_J C_p$$

where $(\partial H/\partial p)_T$ equals the heat which must be supplied to the system per unit of pressure difference to conduct the process isothermally.

When the pressure changes from p to p^*, the heat effect is determined by the change in the enthalpy when the gas passes from the given state to a vacuum, i.e.

$$H^\circ - H = \int_0^p \mu_J C_p \, dp$$

* The process will be isothermal only conditionally, since the substance being throttled has the same temperature only in its initial and final states.

or in accordance with Eq. (6.39)

$$\left(\frac{\partial \ln f}{\partial T}\right)_p = \frac{1}{RT^2}\int_0^p \mu_J C_p \, dp \tag{6.55}$$

It is easy to find the temperature dependence of fugacity with the aid of this equation.

6.5. CALCULATION OF PROPERTIES OF GASES ACCORDING TO EXPERIMENTAL DATA

The properties of gases can be calculated by an equation of state. Thus, for calculating the enthalpy and the heat capacity of a gas under pressure, the equations

$$H_p - H_p^\circ = \frac{9}{128}\frac{RT_{cr}}{p_{cr}}\left(1 - 18\frac{T_{cr}^2}{T^2}\right)p \tag{6.56}$$

and

$$C_p - C_p^\circ = \frac{81}{32}\frac{RT_{cr}^3}{p_{cr}T^2}p \tag{6.57}$$

are used, obtained from Eq. (6.20) on the basis of the general thermodynamic relationships (4.23) and (4.24). Equations (6.56) and (6.57) are accurate only for comparatively low pressures.

In addition to the insufficient reliability of the results and the time-consuming nature of the calculations, insurmountable difficulties also appear. Thus, the comparatively accurate equation (6.21) for an adiabatic process cannot be integrated.

This is why it is good to use a different method to find the properties of substances and draw up thermodynamic tables and diagrams: experimentally studying certain properties and using the relevant equations to calculate the remaining ones. It is desirable here to use a minimum of experimental data.

The existence of several variants of calculations makes it possible to control the results of the calculations and check the reliability of various experimental data.

6.5.1. Calculations Using the Relationships *p-V-T* and $C_p = \varphi(T)$

The experimental data obtained as a result of studying the compressibility of gases within a broad range of temperatures and pressures are usually summarized in tables of the **compression**

factors

$$Z = \frac{pV}{RT} \tag{6.58}$$

and

$$Z' = \frac{pV}{(pV)_0} \tag{6.59}$$

where $(pV)_0$ is the product of the pressure and the volume at $p = 1$ atm and $t = 0\,°C$.

It follows from these equations that $Z/Z' = 273.2/T$ (if we consider that $Z = 1$ at $p = 1$ and $T = 273.2$ K, which usually does not cause errors exceeding 1%).

Equations (6.58) and (6.59) can be considered as equations of state of a real gas. For an ideal gas, $Z = 1$; hence Eq. (6.7) is, as it were, a particular form of Eq. (6.58). The condition that $Z = 1$, however, is not an adequate criterion of the ideal nature of a gas (see also Figs. 31 and 39). In addition to the simplicity of Eqs. (6.58) and (6.59), the compression factors are conveniently dimensionless, and therefore their numerical values are identical in all systems of units. The values of these factors for a given substance, for example, are used to calculate the volume of a gas extracted from the reservoir or tank where it has been stored under pressure, to determine the rate of flow of a gas, to assess the reserves of natural gas, the yield of oil wells, etc. It is especially expedient to use the compression factors in large-scale calculations. Here plots of Z against p and T are also useful.

The p-V-T-x-data for gas mixtures, as for pure gases, can be calculated according to the compression factors for the mixture

$$Z_{av} = \frac{pV}{RT\Sigma n_i} \tag{6.60}$$

where V = total volume of the mixture
n_i = number of moles of the i-th component.

A dependence of Z_{av} on the temperature, pressure and concentration that can be used to find the properties of a gas mixture is known only for a rather small number of binary and ternary mixtures. Therefore, when no experimental data are available, it is possible to use the approximate equation

$$Z_{av} = \frac{\Sigma n_i Z_i}{\Sigma n_i} = \Sigma x_i Z_i \tag{6.61}$$

which is based on the assumption that the volumes are additive. Indeed, if all the volumes are related to the same temperature and a common pressure, then the combination of Eqs. (6.60) and (6.61) gives Eq. (6.12), in which V_i is calculated according to Eq. (6.16).

Calculation of enthalpy, heat capacity and other properties requires that we have at our disposal values of $(\partial V/\partial T)_p$ and other partial derivatives. Their precise determination by direct differentiation, owing to the insignificant curvature of the corresponding lines, is practically impossible [which is especially important to take into account when determining heat capacity, since for finding C_p the derivatives $(\partial V/\partial T)_p$ in accordance with Eq. (4.24) must be differentiated a second time with respect to T and the errors made in the first differentiation may become quite appreciable in the second].

It is convenient to perform graphical differentiation with the aid of a tangentimeter — a metal angle with a mirror surface (Fig. 34). The angle should be arranged so that the mirror image of the section of the curve closest to the given point forms its smooth continuation.

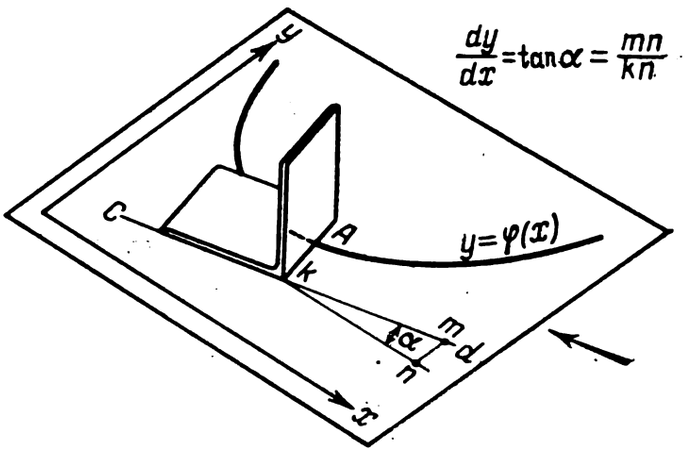

Fig. 34. Graphical differentiation with the aid of a tangentimeter:

ckd = line parallel to a tangent to the curve at point *A*; *kn* = line parallel to the *x*-axis (look along the arrow)

The graduation of the scale selected in plotting the graphs should be such that the errors of graphical smoothing out (this is needed after each intermediate calculation), graphical differentiation and integration are less than the errors of experiment. It is not good to plot a graph to a scale with a very low value of the graduations, since its plotting and processing waste time, while the final results are limited by the accuracy of the experiment.

The partial derivatives of p, V, T can be determined indirectly. It was proposed (E. Deming and L. Schupp) to use the quantities [see Eq. (6.41)]

$$\alpha = V\left(\frac{RT}{pV} - 1\right) = V\left(\frac{1}{Z} - 1\right)$$

and

$$\Delta = V\left(\frac{pV}{RT} - 1\right) = V(Z-1) = -\alpha Z \qquad (6.62)$$

because the curves $\alpha = \varphi(T)$ and $\Delta = \varphi(T)$ are distinguished by a considerable curvature.

The values of $(\partial V/\partial T)_p$ for a given gas can be calculated [see Eqs. (6.41) and (6.62)] from the equations

$$\left(\frac{\partial \alpha}{\partial T}\right)_p = \left(\frac{R}{p}\right) - \left(\frac{\partial V}{\partial T}\right)_p$$

and

$$\left(\frac{\partial \Delta}{\partial T}\right)_p = \left(\frac{\partial V}{\partial T}\right)_p \frac{2pV}{RT} - \frac{pV^2}{RT^2} - \left(\frac{\partial V}{\partial T}\right)_p$$

which are usually written down as follows:

$$\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{RT}{pV} + \frac{1}{TV}\left(\frac{\partial \alpha}{\partial T^{-1}}\right)_p = \frac{1}{Z} + \frac{1}{TV}\left(\frac{\partial \alpha}{\partial T^{-1}}\right)_p$$

and

$$\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{pV/RT - (\partial \Delta/\partial T^{-1})_p/TV}{2pV/RT - 1} = \frac{Z - (\partial \Delta/\partial T^{-1})_p/TV}{2Z - 1}$$

The values of Z (or Z') are used to calculate the values of α and Δ. The data obtained are graphically smoothed out with respect to p (or ρ), after which the values of $(T/V)(\partial V/\partial T)_p$ are calculated by the above equations. Next the values of these quantities obtained in both ways are plotted on a graph and are consecutively smoothed out with respect to p and T.

The quantity $(\partial V/\partial p)_T$ can be found by the equation

$$-\frac{p}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{-pV/RT - (p/V)(\partial \Delta/\partial p)_T}{2pV/RT - 1} = \frac{1}{Z} + \frac{p}{V}\left(\frac{\partial \alpha}{\partial p}\right)_T$$

which is derived in a similar way to that used in deriving the two preceding equations.

The applicability of this method of calculations depends on the accuracy of the p-V-T-data. A. Rozen showed that calculations give reliable results only when the deviation δ of the smoothed out volumes from a linear relationship is large in comparison with the experimental error δ_{exp} within the interval of the conditions being considered (V_1, T_1-V_2, T_2).

This condition is especially significant when calculating C_p, since in accordance with Eq. (4.24) it is necessary to perform two-fold integration, which gives a result other than zero only when the isobars $V = \varphi(T)$ are curved. The quantity δ_{max} can be considered as a measure of the deviation of the isobars from a straight line. Hence the condition

$$\frac{\delta_{exp}}{\delta_{max}} \ll 1$$

will be a criterion showing whether or not the p-V-T-data may be used for calculating C_p.

The results of calculating C_p may be considered reliable only when the errors of experiment become several per cent of the corrected value (not over 10-15%).

For hydrogen, for example, this is not justified. Consequently, the values of $(C_p)_{H_2}$ found by Deming and Schupp are more than doubtful. The anomalous pressure dependence of C_p on C_V for carbon monoxide at low temperatures (with two peaks) which they established is also incorrect.

The requirements for the calculation of enthalpy are less strict; the part of δ is played by the quantity $\delta' = V - V_1(T/T_1)$; here δ' is greater than δ.

The lowest accuracy is needed in determining entropy. Here deviation from proportionality, and not deviation from a straight line, is of importance.

The practical value of the functions Δ and α with observance of the above condition is limited by an additional requirement: the terms with the derivatives $(\partial\Delta/\partial T^{-1})_p$ and $(\partial\alpha/\partial T^{-1})_p$ should form only a fraction of the right-hand side of the equations used for the calculations. Only in this case will the errors made in finding these derivatives not be completely included in $(\partial V/\partial T)_p$. For a number of gases, however (for example for NH_3 and CH_4), the absolute value of these terms exceeds the entire right-hand side of the equations. In such cases, it is good to use direct differentiation of δ (or V) with respect to T.

Rozen (1945) developed a method of calculating the properties of gases based on the **deviation factors** μ_V, μ_p and μ_T, which are, respectively, the ratios of the derivatives $(\partial p/\partial T)_V$, $(\partial V/\partial T)_p$ and $(\partial V/\partial p)_T$ for real gases to the same derivatives for an ideal gas, i.e. respectively to R/V, R/p and $-RT/p^2$. Rozen's method permits us, at least in form, to retain a number of simple relationships of the thermodynamics of ideal gases, for instance the equation of an adiabat, for a real gas.

Being simple, accurate and clear (since the deviations from the laws of ideal gases figure in an explicit form), Rozen's method is very important in the thermodynamics of high pressures, in particular for calculations of multiple-stage compressors.

Since the relationship p-V-T is not a characteristic function (see Sec. 5.2), additional data are needed for calculations. We shall use the relationship $C_{p=1} = \varphi(T)$, which is known as a rule.

Hence according to the found values of $(\partial^2 V/\partial T^2)_p$ on the basis of Eq. (4.24), we have

$$C_p = C_{p=1} - T\int_1^p \left(\frac{\partial^2 V}{\partial T^2}\right)_p dp \qquad (6.63)$$

and we can calculate C_p for high pressures.

The values of C_V can be found from the equations

$$\left.\begin{aligned} C_p &= C_V + T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p \\ \text{or} \quad C_p &= C_V - \frac{T(\partial p/\partial T)_V^2}{(\partial p/\partial V)_T} \end{aligned}\right\} \tag{6.64}$$

The first is obtained by differentiating Eq. (4.16) with respect to V with $T = \text{const}$ and the following combination with Eq. (4.18), and the second is obtained from the first on the basis of Eq. (1.8) as applied to the relationship $\varphi(p, V, T) = 0$.

The Joule-Thomson coefficient is calculated by Eq. (6.50), which in accordance with Eq. (6.41) can be written down as follows:

$$\mu_J = \frac{\alpha - T(\partial\alpha/\partial T)_p}{C_p}$$

The accuracy of the values of μ_J is less than that of the values of $(\partial V/\partial T)_p$ and V, since the numerator of Eq. (6.50) is the difference of these two quantities.

The fugacity is calculated by Eq. (6.42) or by the equation

$$\ln\frac{f}{p} = \ln\gamma = -\int_0^p (1 - Z)\frac{dp}{p} \tag{6.65}$$

which is derived by integrating the equation obtained, in turn, by combining Eqs. (6.33) and (6.58).

The Gibbs energy related to the standard state is calculated by Eq. (6.36).

The Helmholtz energy A related to the standard state is calculated in accordance with Eqs. (5.19) and (6.7) by the equation

$$A_{p,T} - A^\circ_T = (G_{p,T} - pV) - (G^\circ_{p,T} - RT) \tag{6.66}$$

The entropy in accordance with Eqs. (4.21), (4.19) and (6.42) is determined by the equation

$$S_{p,T} - S^*_{T_0} = \int_{T_0}^{T} C^\circ_p\, d\ln T - \int_0^p \left(\frac{\partial V}{\partial T}\right)_p dp =$$

$$= \int_{T_0}^{T} C^\circ_p\, d\ln T + \int_0^p \left[\left(\frac{\partial\alpha}{\partial T}\right)_p - \frac{R}{p}\right] dp \tag{6.67}$$

The enthalpy by Eqs. (3.11), (4.23) and (6.58) equals

$$H_{p,T} - H^{\circ}_{T_0} = \int_{T_0}^{T} C^{\circ}_p \, dT + \int_0^p V\left[1 - \frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_p\right]dp =$$

$$= \int_{T_0}^{T} C^{\circ}_p \, dT - \int_0^p \left(\frac{\partial Z}{\partial T}\right)_p \frac{RT^2}{p} \, dp \qquad (6.68)$$

Finally, in accordance with Eqs. (2.10) and (6.7) we have

$$U_{p,T} - U^{\circ}_{T_0} = (H_{p,T} - pV) - (H^{\circ}_{T_0} - RT_0) \qquad (6.69)$$

Any temperature can be taken as the lower limit in these equations, $T_0 = 273.2$ K being most widely used. The values of entropy and enthalpy are generally represented in a graphical form as H-S and T-S diagrams. Such diagrams are widely used for technological calculations, since many calculations can be reduced to simple reading of the needed value on the diagram.

To illustrate the above material, Figs. 29, 35-38 show some of the results obtained by Ya. Kazarnovsky and the author in processing

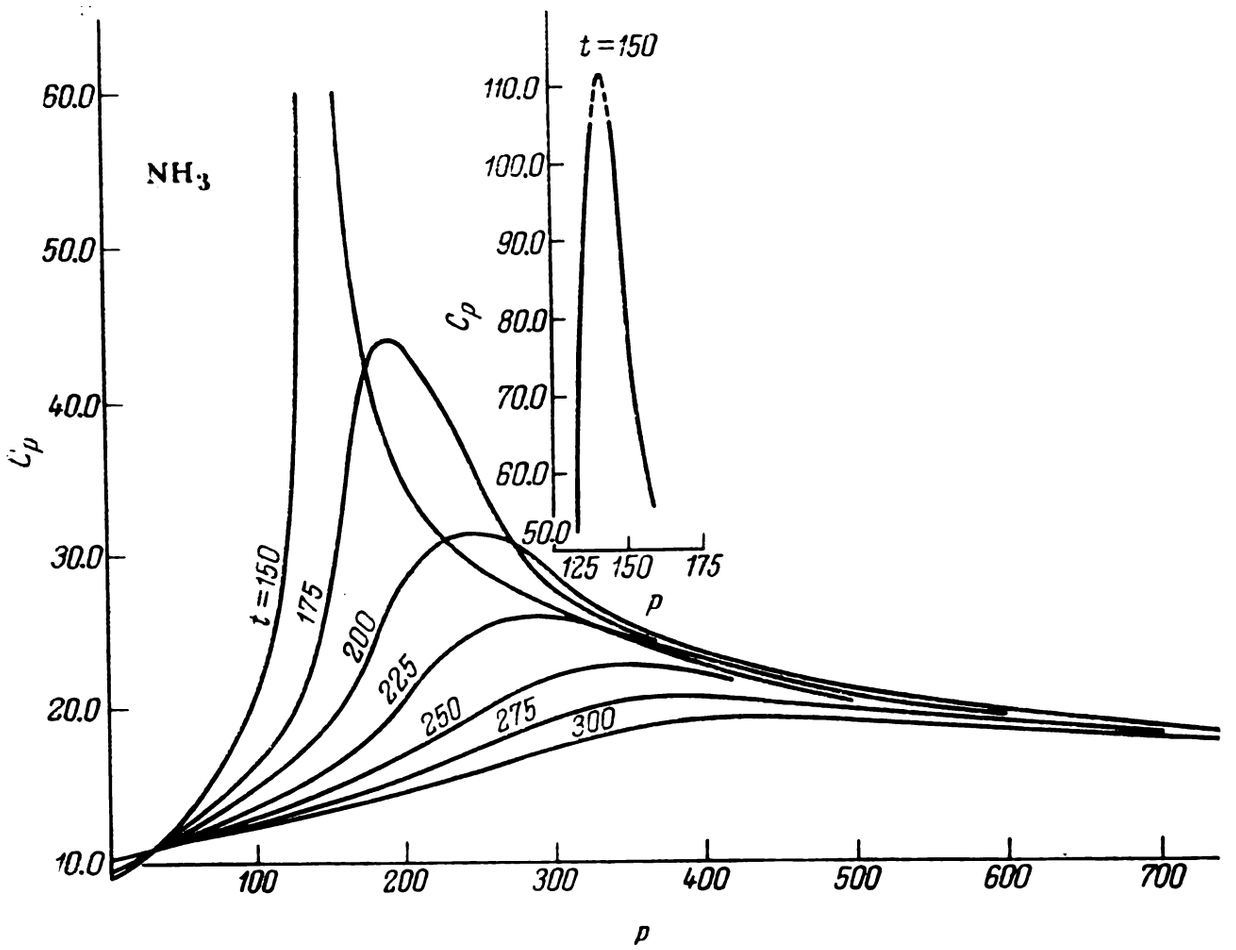

Fig. 35. Dependence of heat capacity of ammonia on temperature and pressure

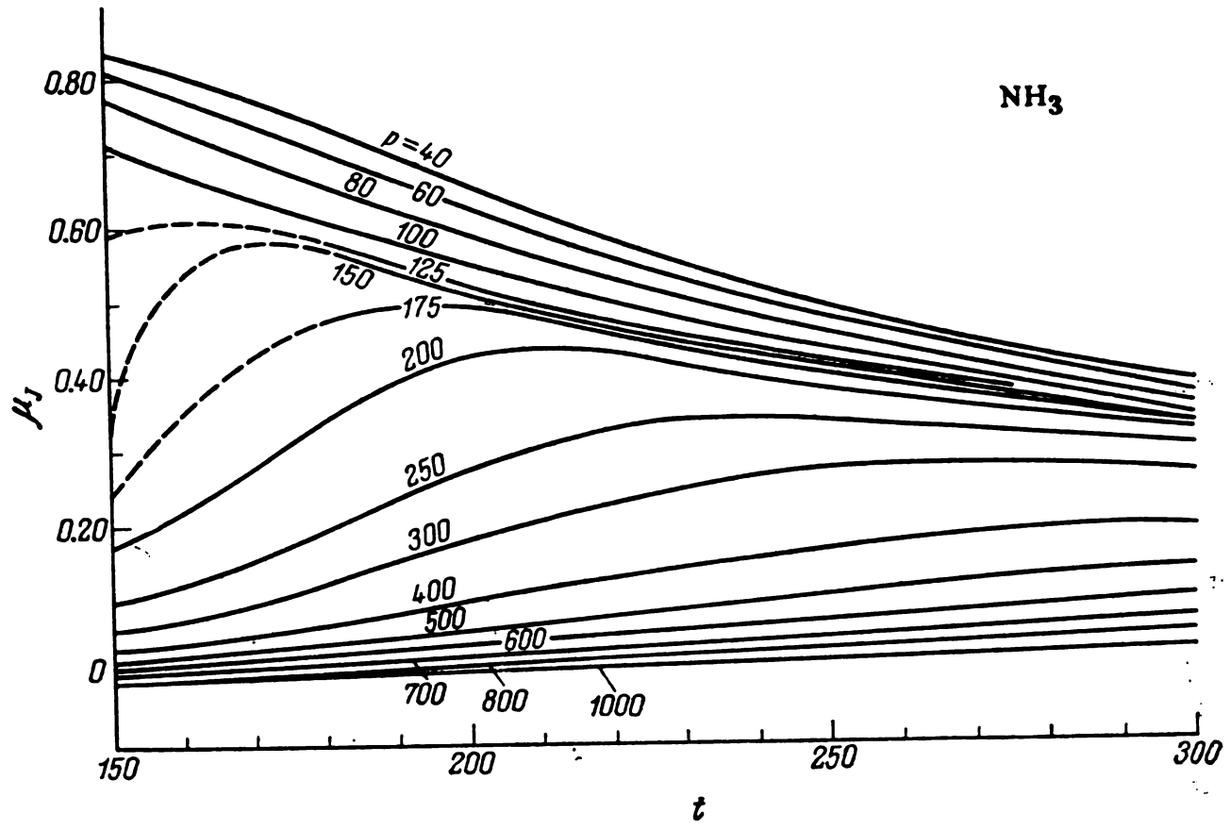

Fig. 36. Dependence of Joule-Thomson coefficient of ammonia on temperature and pressure

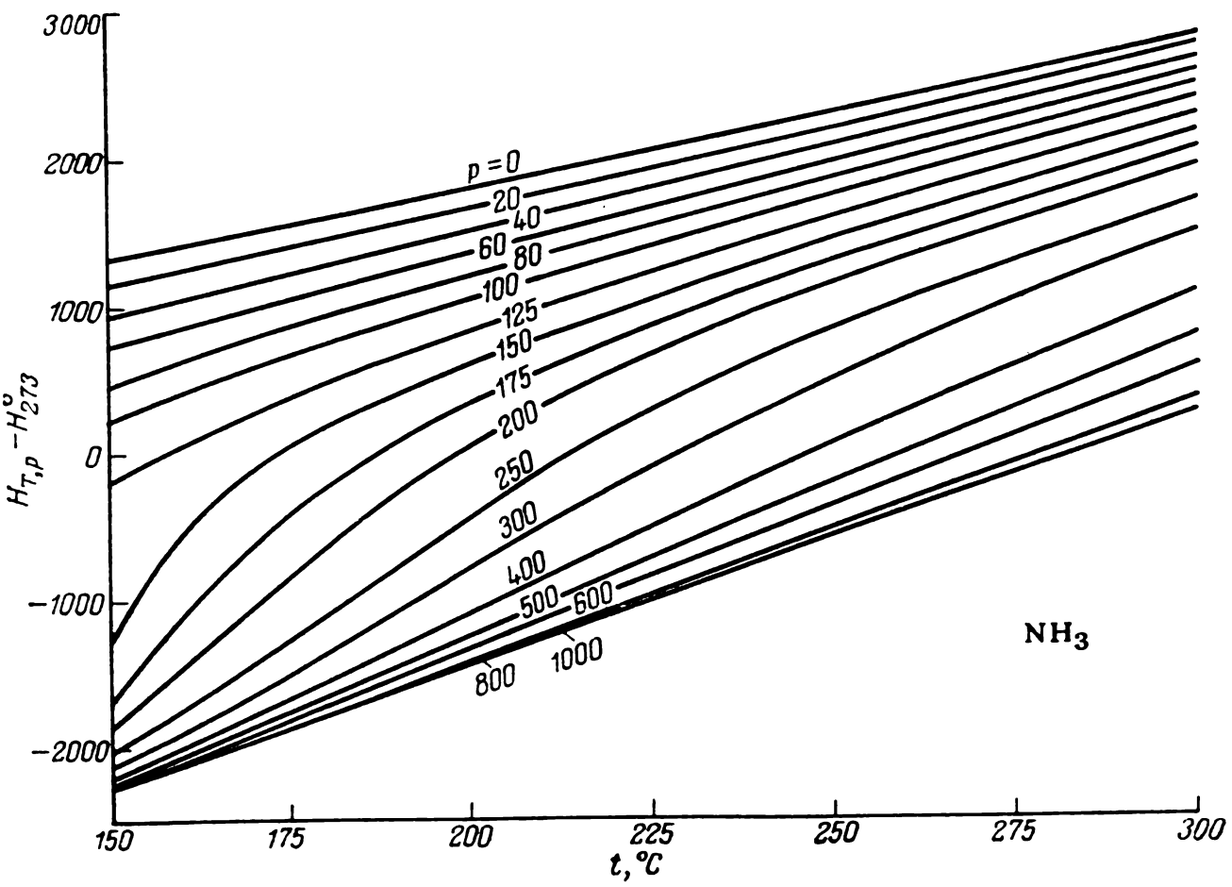

Fig. 37. Enthalpy-temperature diagram for ammonia

experimental data on the compressibility of ammonia within the interval of 150 to 300 °C up to a pressure of 1000 atm. Examination

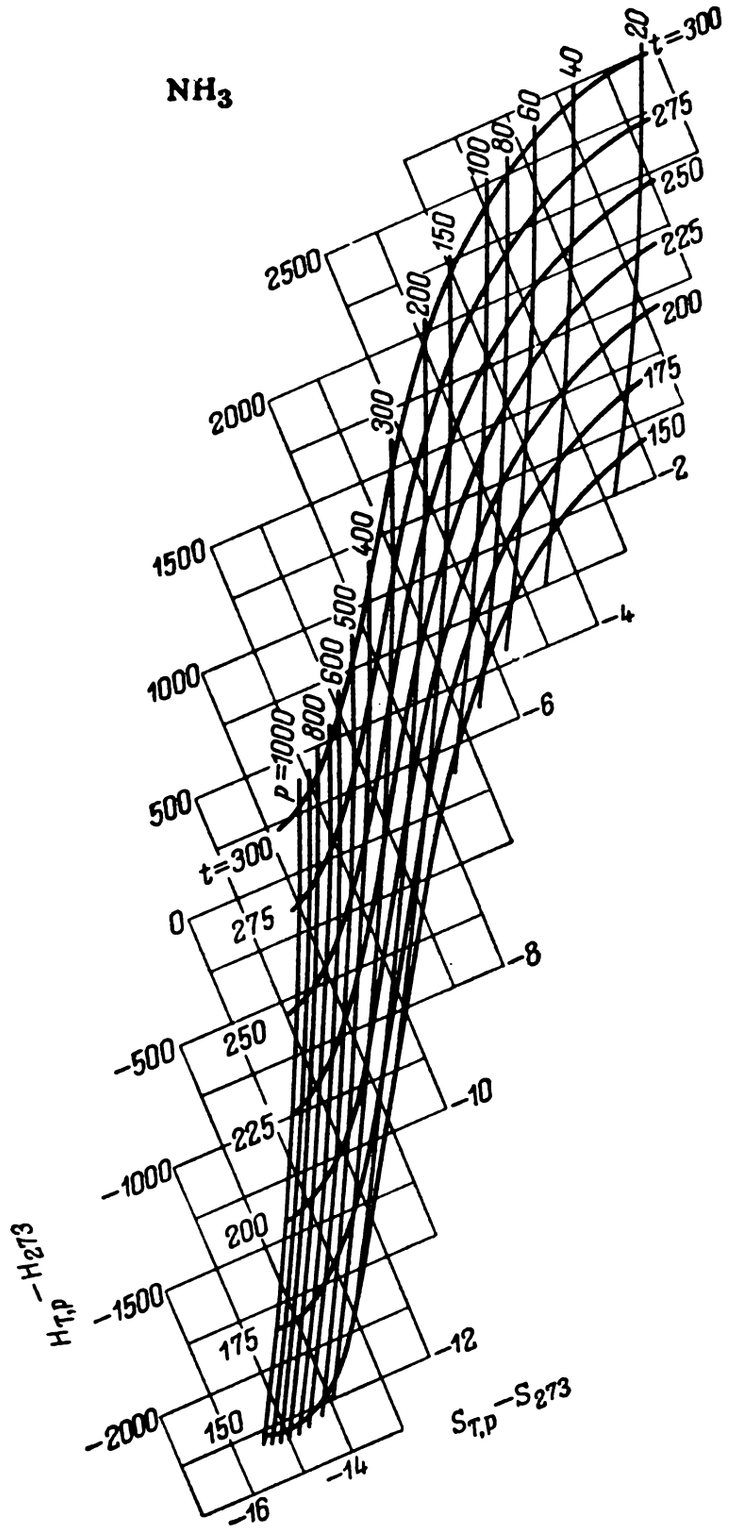

Fig. 38. Enthalpy-entropy diagram for ammonia

of these figures leads us to a number of conclusions. Thus, as already noted, it follows from Fig. 29 (p. 164) that when $p \to 0$, the quantity α tends not to zero, but to a certain constant value. Inspection

of Fig. 35 shows that C_p does not necessarily grow with increasing temperature. It does change quite considerably with a change in p and t in the region close to the critical one (for NH_3 we have $t_{cr} = 132.3\,^{\circ}C$ and $p_{cr} = 111.3$ atm), and is almost independent of p and t at very high pressures. It follows from the same figure that the condition $(\partial C_p/\partial p)_T = 0$ is an essential, but insufficient criterion of the ideal nature of a gas. Figure 36 shows that μ_J diminishes with increasing p and t. Figures 37 and 38 show that H and S grow with an increase in t and diminish with an increase in p.

6.5.2. Calculations Using the Relationships $C_p = \varphi(p, T)$ or $H = \varphi(p, T)$ and $V_T = \varphi(p)$

Having at our disposal the dependence of C_p on p and T, we can find the compressibility of gases by double integration of Eq. (4.24). The integration is conducted graphically or analytically on the basis of the equation

$$V = \varphi(p) + T\varphi'(p) - \overset{T,\ p=\text{const}}{\iint} \frac{1}{T}\left(\frac{\partial C_p}{\partial p}\right)_T dT\ dT$$

where $\varphi(p)$ and $\varphi'(p)$ are arbitrary functions of pressure; their values can be found by the limiting conditions: (a) at $p \to 0$ the value of pV for any temperatures tends to RT; and (b) at $p \to 0$ the value of $[\partial(pV)/\partial T]_p$ for any temperatures tends to R.

If the calculations are based on the values of the enthalpy of the compressed gas, then in accordance with Eq. (4.23)

$$-d\left(\frac{V}{T}\right) = \frac{1}{T^2}\left(\frac{\partial H}{\partial p}\right)_T dT$$

whence at $p = \text{const}$

$$\frac{V}{T} = -\int_{T'}^{T} \frac{1}{T^2}\left(\frac{\partial H}{\partial p}\right)_T dT + \frac{V'}{T'} \qquad (6.70)$$

where V' is the molar volume at the given temperature T' and at the pressure p for which integration is being conducted.

Since calculations according to heat capacity are connected with the transition from second derivatives to an integral, accurate values of V can be obtained by using more accurate values of C_p. (This method is simpler than the preceding one.) It must be noted, however, that for critical and supercritical regions, where C_p changes very sharply (see Fig. 35), direct measurements of the volume are more reliable.

6.5.3. Calculations Using μ_J and C_p

Writing down Eq. (6.50) in the form

$$\frac{\partial}{\partial T}\left(\frac{V}{T}\right)_p = \frac{\mu_J C_p}{T^2}$$

after integration we get

$$\frac{V}{T} = \int_{T'}^{T} \frac{\mu_J C_p}{T^2} dT + \frac{V'}{T'} \tag{6.71}$$

The conformity of the values of μ_J and C_p can be checked by the equation

$$\left(\frac{\partial C_p}{\partial p}\right)_T = \frac{\partial^2 H}{\partial p\, \partial T} = -\left[\frac{\partial(\mu_J C_p)}{\partial T}\right]_p =$$

$$= -\mu_J\left(\frac{\partial C_p}{\partial T}\right)_p - C_p\left(\frac{\partial \mu_J}{\partial T}\right)_p \tag{6.72}$$

which is obtained by combining Eqs. (3.11), (4.23) and (6.50).

The result of this variant of calculating enthalpy can be controlled by the equation

$$\left(\frac{\partial Z}{\partial T}\right)_p = \frac{p}{RT^2}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right] = -\frac{p}{RT^2}\left(\frac{\partial H}{\partial p}\right)_T \tag{6.73}$$

obtained with the aid of Eqs. (4.23) and (6.58).

6.5.4. Influence of Pressure on the Heat Effect of a Reaction

Although this problem relates to the section on multi-component systems, it is expedient to treat it here in connection with the nature of the preceding material.

It follows from Eq. (4.23) that

$$H_{p,T} - H_{p=1,T} = \int_1^p \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp$$

whence

$$\Delta H_{p,T} = \Delta H_{p=1,T} + \int_1^p \Delta V dp - T\int_1^p \left(\frac{\partial \Delta V}{\partial T}\right)_p dp \tag{6.74}$$

The change in ΔH_T with a change in pressure is calculated by Eq. (6.74) from the data on compressibility. Thus, for the reaction

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$$

$$\Delta V = V_{NH_3} - \left(\frac{1}{2}V_{N_2} + \frac{3}{2}V_{H_2}\right)$$

and

$$\left(\frac{\partial \Delta V}{\partial T}\right)_p = \left[\left(\frac{\partial V}{\partial T}\right)_p\right]_{NH_3} - \left\{\frac{1}{2}\left[\left(\frac{\partial V}{\partial T}\right)_p\right]_{N_2} + \frac{3}{2}\left[\left(\frac{\partial V}{\partial T}\right)_p\right]_{H_2}\right\}$$

The values of the volumes and the derivatives can be found by the method set out above. The value of $\Delta H_{p=1,T}$ is calculated by Eq. (3.29). The integrals of Eq. (6.74) are determined graphically.

The pressure appreciably affects ΔH_T when the two integrals of Eq. (6.74) have opposite signs.

Calculations show that the influence of the pressure diminishes with increasing temperature. This is to be expected, because at elevated temperatures the difference in the compressibility of gases does not manifest itself so sharply. At elevated temperatures, however, we can also observe a growth in the heat effect of the synthesis of ammonia by about 20% in comparison with the value of ΔH at normal pressure.

In industrial conditions, the final system contains about 20% of NH_3. Therefore, the results of the calculations should be corrected by ΔH_T of the formation of a nitrogen-hydrogen-ammonia mixture of the composition $0.2N_2 + 0.6H_2 + 0.2NH_3$ from a 1 : 3 nitrogen-hydrogen mixture and ammonia. These calculations can also be performed by Eq. (6.74), considering the heat effect of mixing the gases at atmospheric pressure $\Delta H_{p=1,T} = 0$. Calculations show that the process of mixing N_2, H_2 and NH_3 is endothermic, the action of the pressure being compensated to a considerable extent (Kazarnovsky and the author have established that the maximum difference in ΔH is about 5-10% instead of 20%). This does not mean, however, that the pressure dependence of ΔH_T may be disregarded in all cases and for very great pressures.

6.6. A GENERALIZED METHOD OF CALCULATING SELECTED PROPERTIES OF GASES AND LIQUIDS AT PRESSURES ABOVE ATMOSPHERIC

6.6.1. Gases

It is often impossible to use the methods of calculating the properties of real gases described above because the required data are absent. In this case, a generalized method of calculations can be

used, based on the **principle of corresponding states**. According to this principle, the same *common* function

$$\varphi\left(\frac{p}{p_{cr}}, \frac{V}{V_{cr}}, \frac{T}{T_{cr}}\right) = 0$$

exists for all substances. In other words, if instead of expressing the properties of gases (liquids) through p, V and T, we use dimensionless units for this purpose — the **reduced parameters** $\pi = p/p_{cr}$, $\delta = V/V_{cr}$ and $\tau = T/T_{cr}$, then we can obtain a reduced equation of state $\varphi(\pi, \delta, \tau) = 0$ which contains none of the quantities characterizing a given substance. Such an equation can be obtained from any equation of state having three constants, for example from Eq. (6.19) or (6.20).*

Many important corollaries follow from the principle of corresponding states.** For example, if any two gases have identical values of π and τ, they should occupy an approximately identical reduced volume δ.

Equations with three constants cannot be sufficiently accurate, consequently both the principle of corresponding states and the conclusions following from it are approximate. The errors in calculating various properties do not generally exceed 3-5%, while for similar substances, for example for homologues or for substances with close boiling points, they are considerably smaller.

The necessity thus appears of relieving this principle of a quantitatively inaccurate equation of state with three constants, in particular of Eq. (6.19), which has historically been the basis of the teaching of the corresponding states and its interpretation as the principle of similarity in thermodynamics (dimensionless quantities like the similarity criteria). The teaching of the structure of matter [A49] also apparently enriches this principle.

The application of the principle of corresponding states makes it possible to use the values of π and τ, resorting when necessary to the properties of a gas at $p = 1$ atm, to calculate various properties of gases within a broad range of temperatures and pressures. It is often good to perform the calculations with graphs plotted on the basis of equations relating a given property of a gas to the reduced parameters.

Relationship p-V-T. Considering that all gases in the corresponding states have about the same compression factors, the calculations

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* It should be noted that J. van der Waals's idea of corresponding states was anticipated by D. Mendeleev (1870), who pointed to the usefulness of comparing volumes not at the boiling points, but at temperatures when the cohesion of the liquids is close to zero.

** See, for example, Khvolson, O. D. *Kurs fiziki* (A Course in Physics) (five volumes). Vol. III, Sec. 13.7. Berlin (1933).

can be performed with the aid of a graph of $Z = \varphi(\pi, \tau)$, where φ is a universal function of the reduced parameters (Fig. 39, [C10]). The best coincidence with experimental data for He, H_2 and Ne is obtained when $p_{cr} + 8$ and $T_{cr} + 8$ are substituted for p_{cr} and T_{cr}, respectively. Such a graph is more accurate than that of $\pi = \varphi(\tau)$ containing lines of $\delta = \text{const}$. The latter is convenient for interpolation (because of the virtually linear nature of the reduced isochors), but is inaccurate owing to the unauthentic values of V_{cr} (see p. 224).

It follows from the graph of $Z = \varphi(\pi, \tau)$ that when τ exceeds approximately three, the volume of any gas at any pressure is greater than V_i. Therefore, the statement that the heating of a gas brings it closer to the ideal state is not always correct. For all gases when π exceeds nine, we have $Z > 1$ for all temperatures, and as the temperature grows, Z approaches unity. When $Z = 1$ ($\gamma = 1$), however, a gas is not ideal, since a slight change in p (or T) is sufficient for violation of this equation.

The same method can be used for the approximate calculation of the compressibility of a mixture: the latter is considered as an ideal gas having the average molecular weight and characterized by the pseudocritical pressure and temperature expressed by the equations *

$$T'_{cr} = x_1(T_{cr})_1 + x_2(T_{cr})_2 + \ldots \tag{6.75}$$

and

$$p'_{cr} = x_1(p_{cr})_1 + x_2(p_{cr})_2 + \ldots \tag{6.76}$$

After their calculation, Fig. 39 can be used to find the mean compression factor of the mixture, and the volume of the mixture can then be calculated. If p and V (or T and V) are given, the calculations are conducted by trial and error.

Example 11.** Calculate the pressure needed to compress 0.8 dm^3 of methanol vapour at a pressure of $p = 60$ atm and a temperature of $t = 350\,°C$ to a volume of 0.0907 dm^3 at 250 °C.

Solution. The initial conditions correspond to values of $\tau_1 = 1.21$ and $\pi_1 = 0.762$. From Fig. 39 we find $Z_1 = 0.85$. The final conditions are $\tau_2 = 1.02$ and $\pi_2 = p/78.7$. Applying Eq. (6.58) to a gas in two different states, we get $p_1V_1/p_2V_2 = Z_1T_1/Z_2T_2$, whence

$$Z_2 = \frac{p_2 \times 90.7 \times 0.85 \times 623.2}{60 \times 800 \times 523.2} = 0.001\,89p_2$$

* Higher values of T and p, as a rule, correspond to the true critical point (see Chap. 10).

** Take the values of the critical parameters needed to solve Examples 11-17 from Appendix 9.

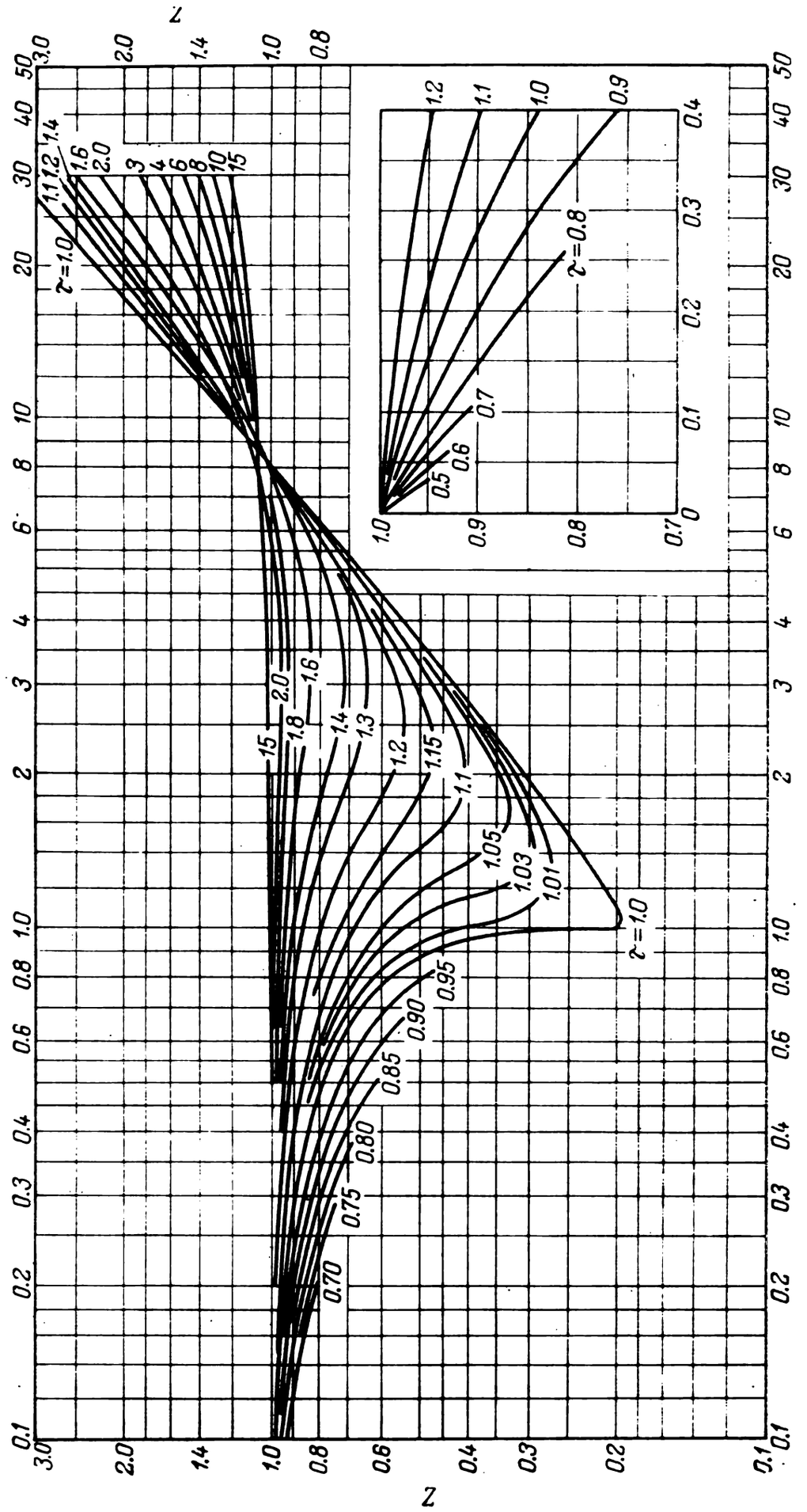

Fig. 39. Dependence of compression factors of gases on the reduced pressure and temperature [C10].

(See Examples 11-14)

and

$$Z_2 = 0.001\,89 \times 78.7\pi_2 = 0.149\pi_2$$

Hence, a straight line should be drawn in Fig. 39 that corresponds to the obtained equation $Z_2 = \varphi(\pi_2)$. Since both coordinates of the graph have an equal logarithmic scale, this line should have a slope of 45 degrees (it follows from the equation $Z = C\pi$ that $\log Z = \log C + \log \pi$). In addition, it should pass through the point with the coordinates $Z = 0.149$ and $\pi = 1.0$ and through the point with the required values of τ_2 and π_2. We find the position of the latter by continuing the straight line to its intersection with the isotherm $\tau_2 = 1.02$. The point of intersection gives $Z_2 = 0.4$ and $\pi_2 = 2.8$. Hence, $p_2 = 2.8 \times 78.7 = 220$ atm. The experimental value is $p_2 = 250$ atm.

Example 12. The volume occupied by 1 kg of propane at $p = 100$ atm equals 7.81 dm³. Determine the temperature of the gas with the aid of Fig. 39.

Solution. $\pi = 2.38$; $V = 7.81 \times 44.06 = 344.1$. By Eq. (6.58) we have $100 \times 344.1 = Z \times 82.06\tau \times 370.0$, whence $Z = 1.13/\tau$. Further, using the data of Fig. 39, we plot Z against τ for $\pi = 2.38$. The point of intersection of the curve obtained in this way with the curve $Z = 1.13/\tau$ gives us the required value of $\tau = 1.45$. Hence $T = 369.9 \times 1.45 = 536.4$ K ($t = 263.2$ °C), which differs from the experimentally found value (253.2 °C) by 10 kelvins.

Example 13. Determine the density of one mole of a mixture consisting of 25.4% of C_2H_4 and 74.6% of O_2 at $t = 25$ °C and $p = 100$ atm with the aid of Fig. 39.

Solution. According to the data given in Appendix 9, we find $\tau = 1.056$ and $\pi = 2.0$ for C_2H_4, and $\tau = 1.93$ and $\pi = 2.01$ for O_2; next from Fig. 39 we find $Z = 0.35$ for C_2H_4 and $Z = 0.95$ for O_2, and by Eq. (6.61) we get $Z_{av} = 0.254 \times 0.35 + 0.746 \times 0.95 = 0.80$.

The volume of the mixture by Eq. (6.60) is $V = (1 \times 0.80 \times \times 82.06 \times 298.2)/100 = 196$ and the density $\rho = 0.0051$ (the experimentally found value is 0.0046).

Example 14. Using the method of pseudocritical parameters, find the pressure under which a mixture consisting of 17.6% of NH_3, 20.6% of N_2 and 61.8% of H_2 should be for one mole to occupy a volume of 112.5 cm³ at $t = 200$ °C.

Solution. According to Eqs. (6.75) and (6.76) the pseudocritical parameters are

$$T'_{cr} = 0.176 \times 405.5 + 0.206 \times 123.3 + 0.618 \times 41.3 = 122.3$$

and

$$p'_{cr} = 0.176 \times 111.3 + 0.206 \times 38.5 + 0.618 \times 20.8 = 40.4$$

The pseudoreduced parameters are

$$\tau = \frac{473.2}{122.3} = 3.87 \text{ and } \pi = \frac{p}{40.4}$$

The required pressure p is determined by trial and error. Taking $p = 404$ atm ($\pi = 10$), from Fig. 39 we find $Z \approx 1.15$, i.e. $V = (1.15 \times 82.06 \times 473.2)/404 = 110.5$, which almost coincides with $V = 112.5$; we finally assume that $p = 395$ atm, which differs from the experimentally found value of the pressure (400 atm) by 1.3%.

Fugacity. Assuming the unambiguity of the function $\gamma = \varphi(\pi, \tau)$, we can construct graphs on which lines of $\tau = \text{const}$ are plotted in the coordinates $\gamma = \varphi(\pi)$. It will be found that the reduced isotherms approximately coincide for all gases. This method was verified for 24 gases; for H_2, He and Ne the quantities $(p_{cr} + 8)$ and $(T_{cr} + 8)$ must be used instead of p_{cr} and T_{cr}.

A graph of $\gamma = \varphi(\pi, \tau)$ is shown in Fig. 40 [C10]. It was based on the data shown in Fig. 39 and found by the equation

$$\ln \gamma = \int_0^{\pi} \frac{Z - 1}{\pi} d\pi \tag{6.77}$$

obtained from Eq. (6.65) by substituting $p_{cr}\pi$ for p. The values of γ are also given in Appendix 8.

In Figs. 39 and 40, the curves $\tau = \text{const}$ for $\pi = 0$ give $Z = 1$ and $\gamma = 1$, respectively, since regardless of the temperature, at $p \to 0$ gases behave like ideal ones.

Enthalpy. If in Eq. (6.73) we express p and T by π and τ, we get

$$\left(\frac{\partial H}{\partial \pi}\right)_T \frac{1}{p_{cr}} = -\frac{R\tau^2 T_{cr}^2}{\pi p_{cr} T_{cr}} \left(\frac{\partial Z}{\partial \tau}\right)_p$$

After cancellation, we integrate at $T = \text{const}$ within the limits from the pressure at which the enthalpy does not depend on the pressure (ideal gas) to a high pressure. The result is

$$\frac{H - H^\circ}{T_{cr}} = -R\tau^2 \int_0^{\pi} \left(\frac{\partial Z}{\partial \tau}\right)_p d \ln \pi \tag{6.78}$$

The values of $(\partial Z/\partial \tau)_p$ needed for calculating the enthalpy of a compressed gas were computed by graphical differentiation according to Fig. 39, after which a graph of $(H^\circ - H)/T_{cr} = \varphi(\pi, \tau)$

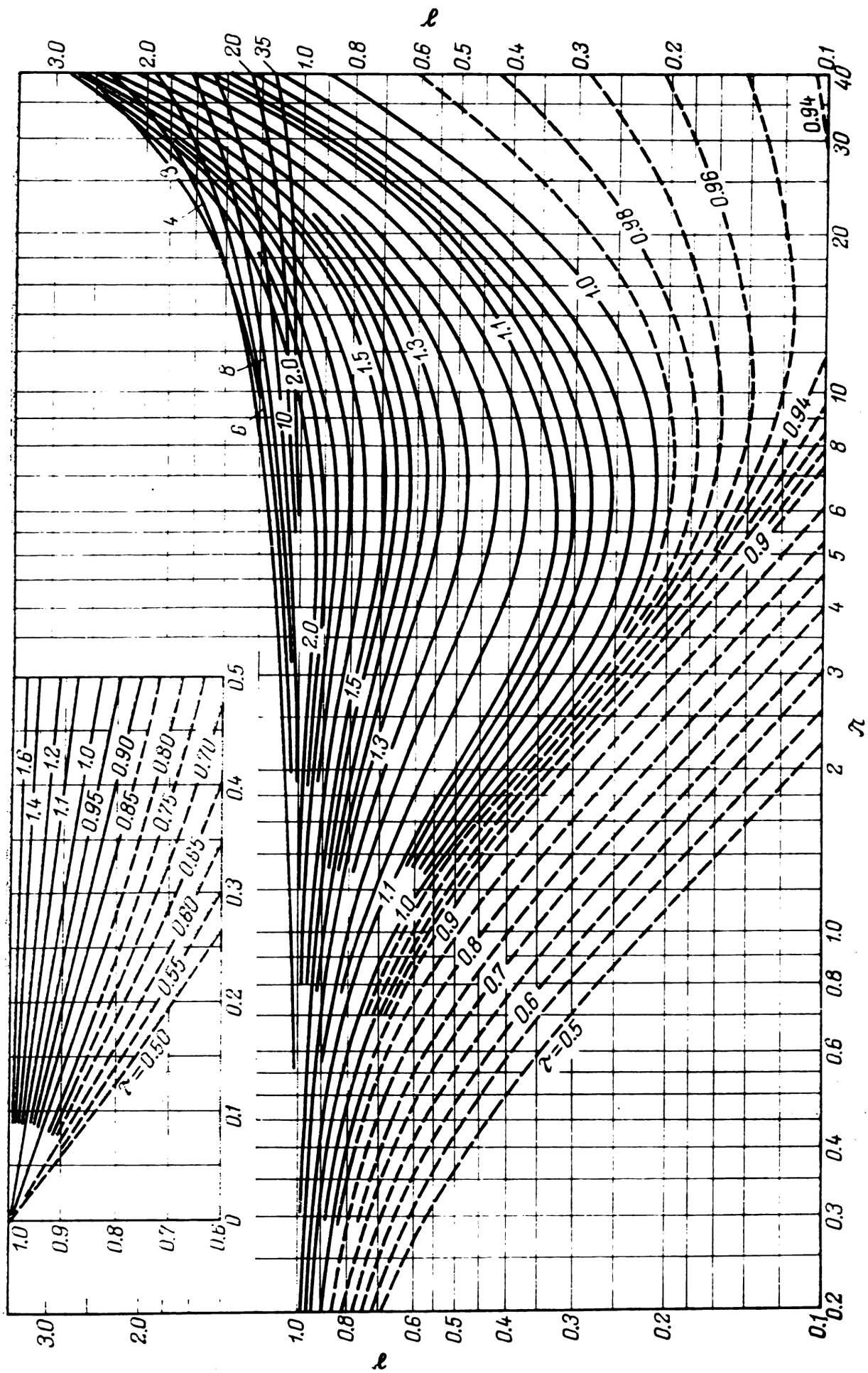

Fig. 40. Dependence of activity coefficient of gases on the reduced pressure and temperature [C10]

was plotted (Figs. 41 and 42 [C10]), which permits us to calculate the change in the enthalpy of a gas when it is compressed from an infinitely low (practically atmospheric) to a high pressure. It was found that a more accurate result (at least for hydrocarbons and water vapour) is obtained when the correction factor Φ is applied to the quantity $H^\circ - H$ in the calculations:

$$\Phi = \left(\frac{T_{cr}}{370}\right)^n$$

The empirical coefficient n depends on τ (this relationship is shown in the top left-hand corner of Fig. 42). The quantity n has not been determined for $\tau < 1$, but its absence in such cases does not result in considerable errors.

Example 15. Find the change in enthalpy when one mole of pentane is compressed from an infinitely low pressure to $p = 34$ atm if $t = 237.8\,^\circ C$.

Solution. In accordance with the values $\pi = 1.03$ and $\tau = 1.09$, from Fig. 42 we find $(H^\circ - H)/T_{cr} = 2.8$, i.e. $H^\circ - H = 1320$. From the same figure $n = 0.26$ and

$$\Phi = \left(\frac{469.8}{370}\right)^{0.26} = 1.064$$

whence

$$H^\circ - H = 1320 \times 1.064 = 1405 \text{ cal/mol}$$

The experimentally found value is $\Delta H = 1430$ cal/mol. In view of the closeness of the critical region, the coincidence is quite good.

Entropy. At $T = \text{const}$, by Eqs. (4.19) and (6.7) we have

$$(S_p^* - S_p)_T = \int_p^0 \left[\frac{R}{p} - \left(\frac{\partial V}{\partial T}\right)_p\right] dp$$

Using in this equation the expression

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{ZR}{p} + \frac{RT}{p}\left(\frac{\partial Z}{\partial T}\right)_p$$

found from Eq. (6.58), we get

$$(S_p^* - S_p)_T = R\int_\pi^0 (1 - Z)d\ln\pi + R\tau\int_0^\pi \left(\frac{\partial Z}{\partial \tau}\right)_p d\ln\pi$$

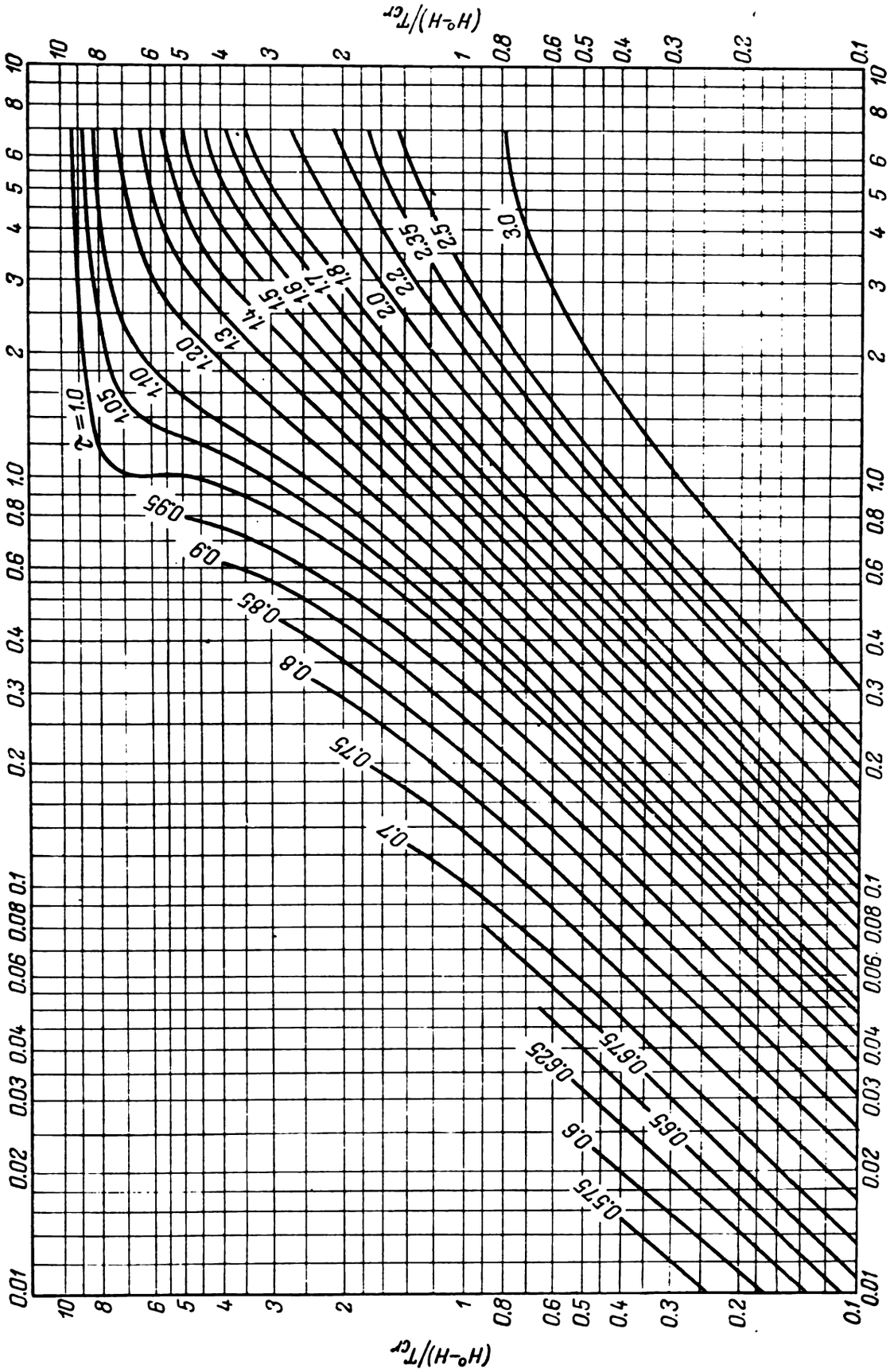

Fig. 41. Dependence of enthalpy of gases on the reduced pressure and temperature [C10] (see also Fig. 42)

or in accordance with Eq. (6.78)

$$(S_p^* - S_p)_T = R\int_{\pi}^{0}(1 - Z)d\ln\pi - \frac{H - H^\circ}{\tau T_{cr}} \qquad (6.79)$$

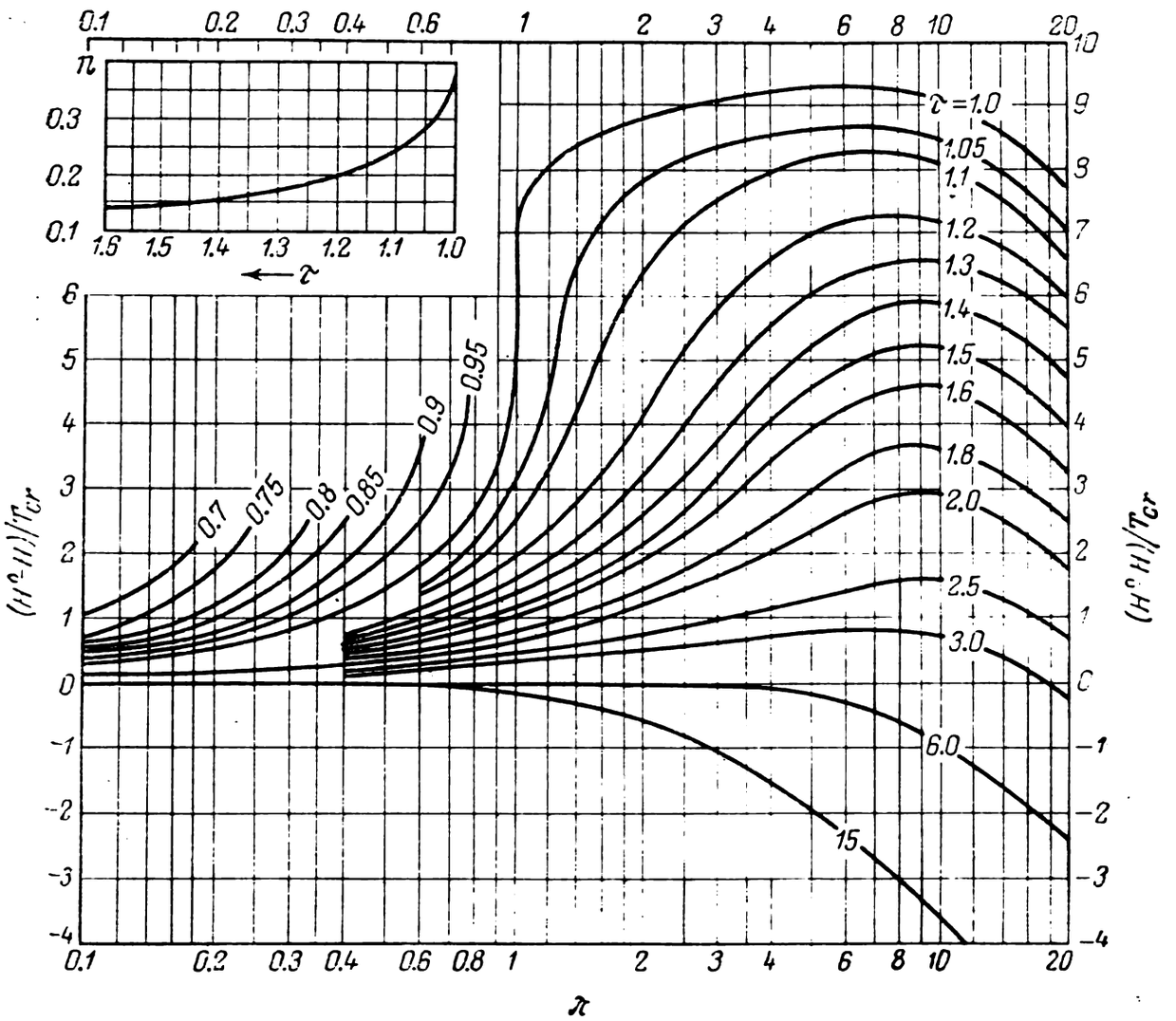

Fig. 42. Dependence of enthalpy of gases on the reduced pressure and temperature [C10] (see also Fig. 41).

(See Example 15)

The value of the first term in the right-hand side of this equation is determined from Fig. 39, and of the second term from Figs. 41 and 42. The values of $(S_p^* - S_p)_T$ are given in Fig. 43 [C10].

Heat Capacity. We shall rewrite Eq. (6.63) in the form

$$(C_p - C_p^\circ)_T = -\frac{\tau}{T_{cr}}p_{cr}\int_{0}^{\pi}\left(\frac{\partial^2 V}{\partial\tau^2}\right)_p d\pi$$

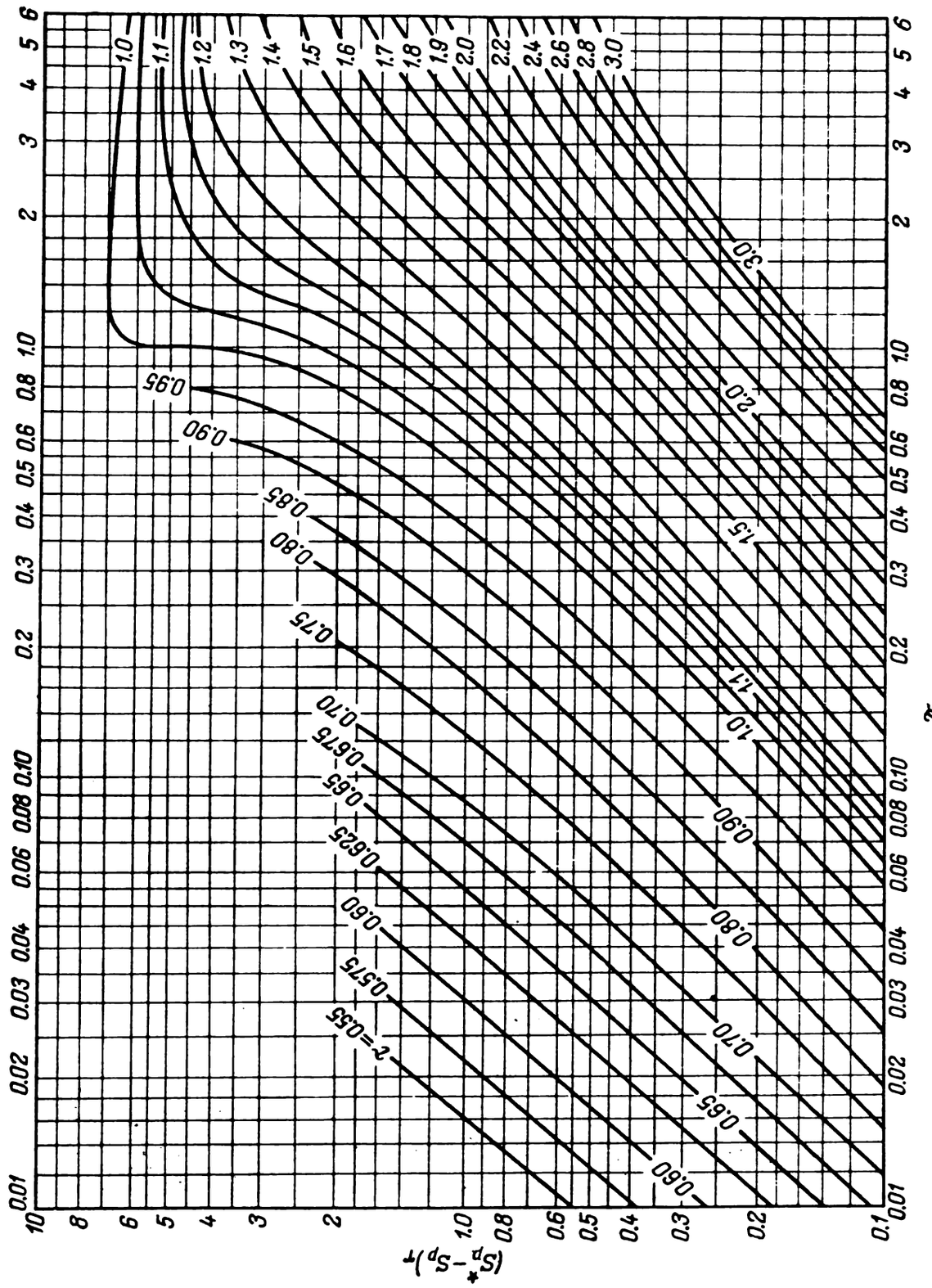

Fig. 43. Dependence of entropy of gases on the reduced pressure and temperature [C10]

To find the quantity $(\partial^2 V/\partial \tau^2)_p$, we shall express p and T in Eq. (6.58) by π and τ. After differentiation, we obtain

$$\frac{p_{cr}}{T_{cr}}\left(\frac{\partial^2 V}{\partial \tau^2}\right)_p = \frac{R}{\pi}\left[\tau\left(\frac{\partial^2 Z}{\partial \tau^2}\right)_p + 2\left(\frac{\partial Z}{\partial \tau}\right)_p\right]$$

therefore

$$(C_p - C_p^\circ)_T = -\tau\int_0^\pi \frac{R}{\pi}\left[\left(\frac{\partial^2 Z}{\partial \tau^2}\right)_p + 2\left(\frac{\partial Z}{\partial \tau}\right)_p\right]d\pi \qquad (6.80)$$

The integrand can be determined by graphical differentiation using Fig. 39.

Since plotting of the graph $C_p - C_p^\circ = \varphi(\pi, \tau)$ involves double differentiation, the error in calculating C_p is much greater than when calculating H and may reach a quite considerable per cent [especially in the critical region (π, $\tau \to 1$) *]. There are little data on $C_p = \varphi(p)$, however, while comparison of the values calculated by processing experimental data on the compressibility of gases (see the preceding section) cannot confirm the calculations, because these values are also insufficiently reliable. For this reason, the author plotted a graph of $C_p - C_p^\circ = \varphi(\pi, \tau)$ (Fig. 44) chiefly using the relationship $H = \varphi(p, T)$ for different gases.

Joule-Thomson Effect. It follows from Eqs. (6.39) and (6.34) that

$$\frac{\partial \ln \gamma}{\partial T} = \frac{H^\circ - H}{RT^2} \quad \text{or} \quad \frac{H^\circ - H}{T} = R\tau\frac{\partial \ln \gamma}{\partial \tau}$$

Since

$$H^\circ - H = (C_p^\circ)_{av}\,\Delta T$$

then

$$\frac{H^\circ - H}{(C_p^\circ)_{av}} = \frac{RT}{(C_p^\circ)_{av}}\frac{\partial \ln \gamma}{\partial \ln \tau} = \Delta T$$

where $(C_p^\circ)_{av}$ = heat capacity between the initial and final temperature of a gas during its throttling

ΔT = change in the temperature when the gas is throttled to such a low pressure that $H \neq \varphi(p)$.

In practice both these quantities can be taken at $p = 1$. Rewriting the last equation in the form

$$\Delta T = \frac{RT_1\tau}{(C_p^\circ)_{av}}\frac{\partial \ln \gamma}{\partial \tau_1} = \frac{RT_1^2}{(C_p^\circ)_{av}T_{cr}}\frac{\partial \ln \gamma_1}{\partial \tau_1} \qquad (6.81)$$

* At the critical point $C_p = \infty$.

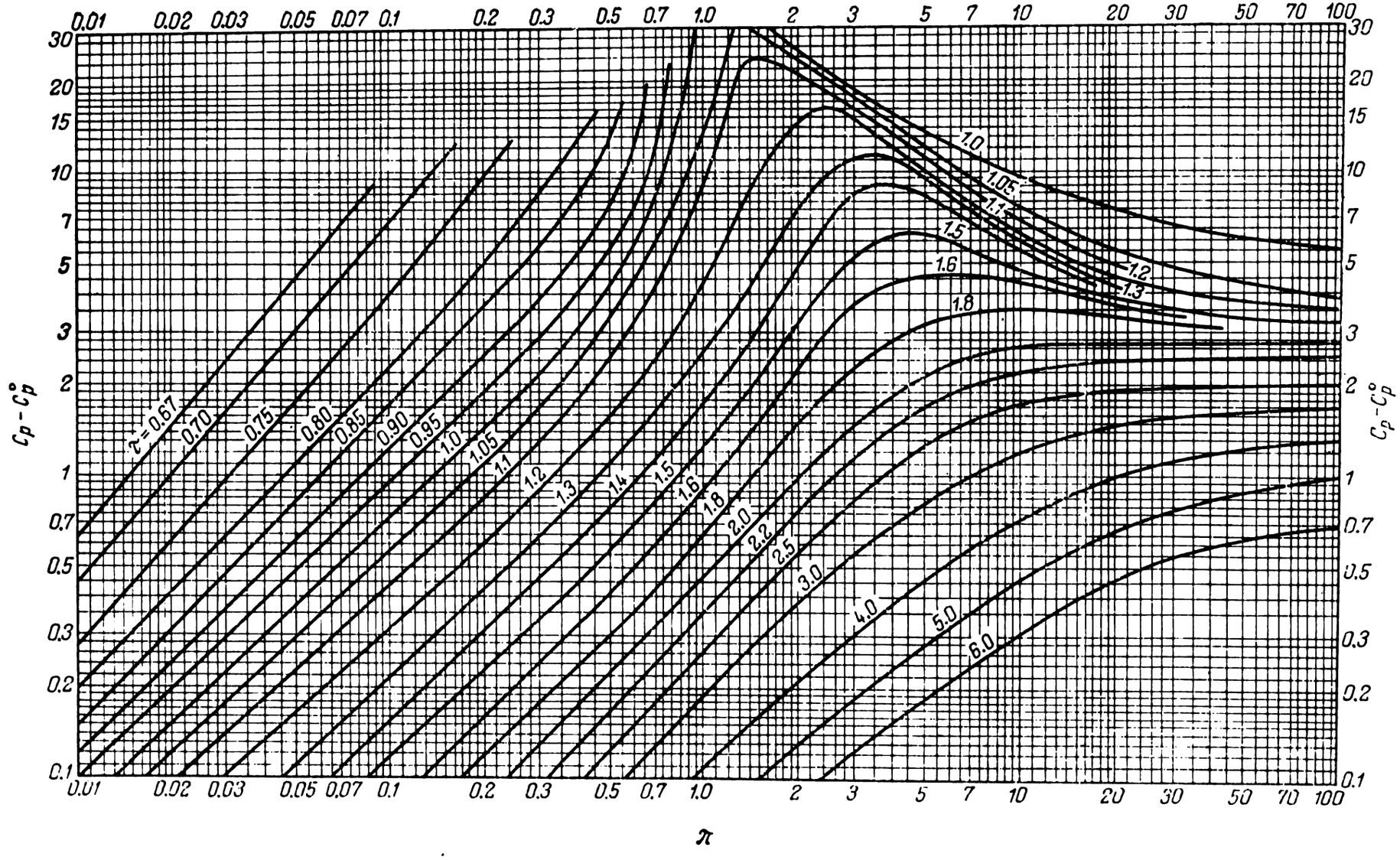

Fig. 44. Dependence of heat capacity of gases on the reduced pressure and temperature

we get

$$\Delta T = \frac{RT_1^2}{(C_p^0)_{av} T_{cr}} \frac{\ln (\gamma_1'/\gamma_1'')}{\tau_1' - \tau_1''} \tag{6.82}$$

In this equation, the quantities γ_1' and γ_1'' relate to the initial pressure and to values of τ_1' and τ_1'' so close to the initial temperature T_1 (one for $T < T_1$ and the other for $T > T_1$) that we can consider the assumption $\partial \ln \gamma / \partial \tau = \Delta \ln \gamma / \Delta \tau$ used to derive Eq. (6.82) from Eq. (6.81) to be true.

Equation (6.81) is sufficiently accurate if we consider a gas to be ideal at p_1. If p_1 is very large, the equation should be altered.

For very approximate calculations, we can also use a reduced inversion curve. The latter can be plotted according to the equation obtained by combining Eq. (6.50) written down in reduced units with an equation of state [for example Eq. (6.19)] also expressed in reduced units.

Example 16. One of the experiments run in studying the throttling of air gave the following results: the initial temperature was 3.2 °C and the corresponding pressure was 185.3 atm; the final pressure was 1.2 atm. Calculate the integral throttling effect with the aid of Eq. (6.82).

Solution. We have $\pi_1 = 4.95$ and $\tau_1 = 2.09$. Taking a small temperature interval ($\tau_1' = 2.2$ and $\tau_1'' = 2.0$), from Fig. 41 we find $\gamma_1' = 0.99$ and $\gamma_1'' = 0.94$. Hence, by Eq. (6.82) we obtain

$$\Delta T = \frac{1.987 \times 276.4^2}{6.95 \times 132.3} \times \frac{2.303 \log \dfrac{0.99}{0.94}}{2.2 - 2.0} = 42.8 \text{ K}$$

The experimentally found value is 39.6 K.

6.6.2. Liquids

The properties of pure liquids (expansion, compressibility, influence of pressure on enthalpy, entropy, heat capacity, etc.) can be determined on the basis of the boiling point, critical temperature, critical pressure and the density of a liquid at a single temperature by the following method [C10].

Relationship p-V-T. Whereas the compression factor Z is approximately the same for all gases at identical values of π and τ, for liquids a similar factor ω, determined from the equation

$$\rho = \frac{pM}{ZRT} = \frac{\pi p_{cr} M}{ZR\tau T_{cr}} = \frac{\pi}{ZR\tau} \frac{p_{cr} M}{T_{cr}} = \omega \frac{p_{cr} M}{T_{cr}} \tag{6.83}$$

fluctuates for various substances up to 20%. Therefore, Eq. (6.83) is roughly approximate.

If we know the density of a liquid ρ for at least one temperature and the relationship $\omega = \varphi(\pi, \tau)$ for a substance, it is better to use the following proportion obtained from Eq. (6.83):

$$\frac{\rho}{\rho_1} = \frac{\omega}{\omega_1} \tag{6.84}$$

in which the subscript 1 indicates the initial state (π_1, τ_1). The values of ω are given in Fig. 45 (plotted according to data for isopentane and propane). The mean error does not exceed 5%.

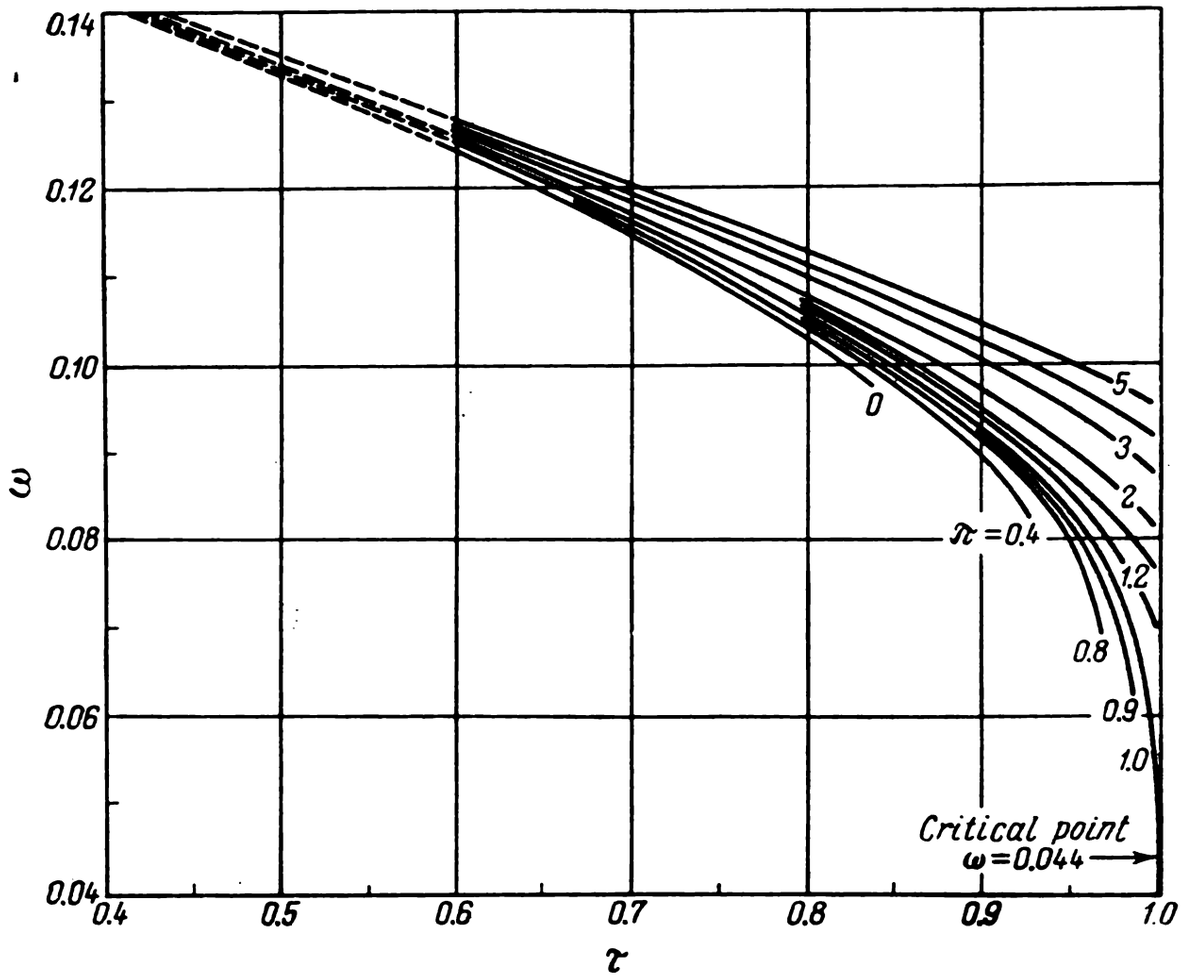

Fig. 45. Dependence of compressibility of a liquid on the reduced pressure and temperature [C10].

(See Example 17)

Enthalpy. Let us combine Eqs. (6.84) and (4.23) after writing them down in reduced parameters. We get

$$\frac{1}{p_{cr}}\left(\frac{\partial H}{\partial \pi}\right)_T = \frac{1}{\rho} - \tau\left(\frac{\partial \rho^{-1}}{\partial \tau}\right)_p = \frac{\omega_1}{\rho_1}\left[\frac{1}{\omega} - \tau\left(\frac{\partial \omega^{-1}}{\partial \tau}\right)_p\right]$$

or after integration within the limits from π to $\pi = 1$

$$\frac{\rho_1}{p_{cr}\omega_1}(H_{p_{cr}} - H)_T = \int_{\pi}^{\pi=1} \left[\frac{1}{\omega} + \frac{\tau}{\omega^2}\left(\frac{\partial\omega}{\partial\tau}\right)_p\right] d\pi \qquad (6.85)$$

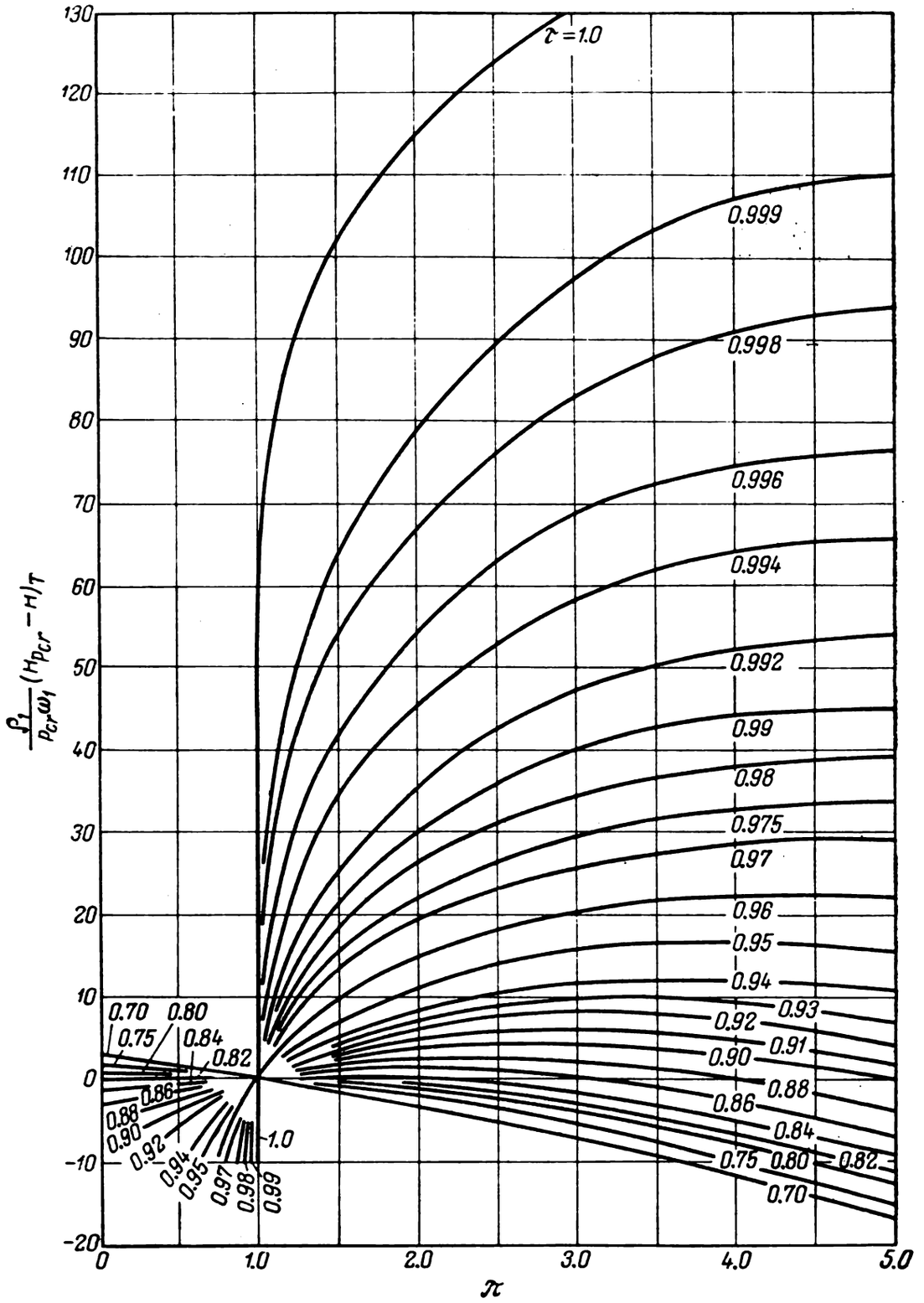

Fig. 46. Dependence of enthalpy of a liquid on the reduced pressure and temperature [C10]

We can perform integration after finding the value of $(\partial\omega/\partial\tau)_p$ from Fig. 45. The results of integration are shown in Fig. 46, which helps us to determine the influence of pressure on the enthalpy of a liquid.

Entropy. The change of S with the pressure is expressed by the equation

$$\frac{T_{cr}\rho_1}{p_{cr}\omega_1}(S_{p_{cr}} - S)_T = \int_{\pi}^{\pi=1} \frac{1}{\omega^2}\left(\frac{\partial\omega}{\partial\tau}\right)_p d\pi \qquad (6.86)$$

which is derived by combining Eqs. (4.19) and (6.84) with the following integration of the equation obtained from π to $\pi = 1$.

Figure 47 gives the results of calculations by this equation.

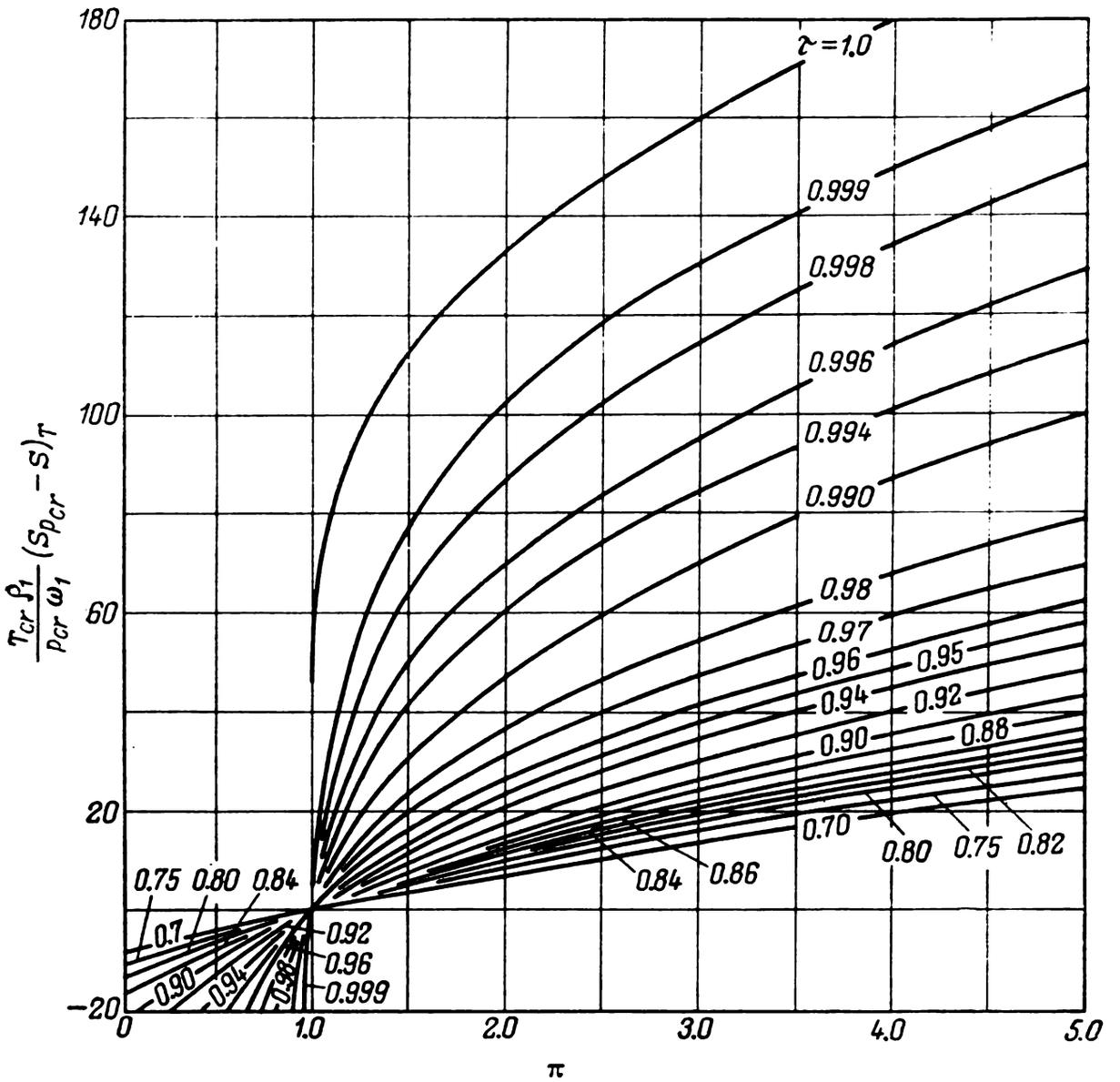

Fig. 47. Dependence of entropy of a liquid on the reduced pressure and temperature [C10]

Heat Capacity. The influence of pressure on C_p is determined as follows. Denoting the left-hand side of Eq. (6.85) by Ψ, we differentiate the resulting equation (for p = const) and get

$$\frac{\rho_1}{p_{cr}\omega_1}\left[\left(\frac{\partial H_{p_{cr}}}{\partial T}\right)_p - \left(\frac{\partial H}{\partial T}\right)_p\right]_T = \frac{1}{T_{cr}}\left(\frac{\partial \Psi}{\partial \tau}\right)_p$$

or

$$\frac{T_{cr}\rho_1}{p_{cr}\omega_1}(C_{p_{cr}} - C_p)_T = \left(\frac{\partial \Psi}{\partial \tau}\right)_p \qquad (6.87)$$

The results corresponding to this equation are shown in Fig. 48.

Equations (6.85), (6.86) and (6.87) or their corresponding graphs can be used to calculate the change in the quantities proportional to H, S and C_p, respectively, when passing from p_{cr} ($\pi = 1$) to different values of π (within the limits from $\pi = 0$ to $\pi = 5$).

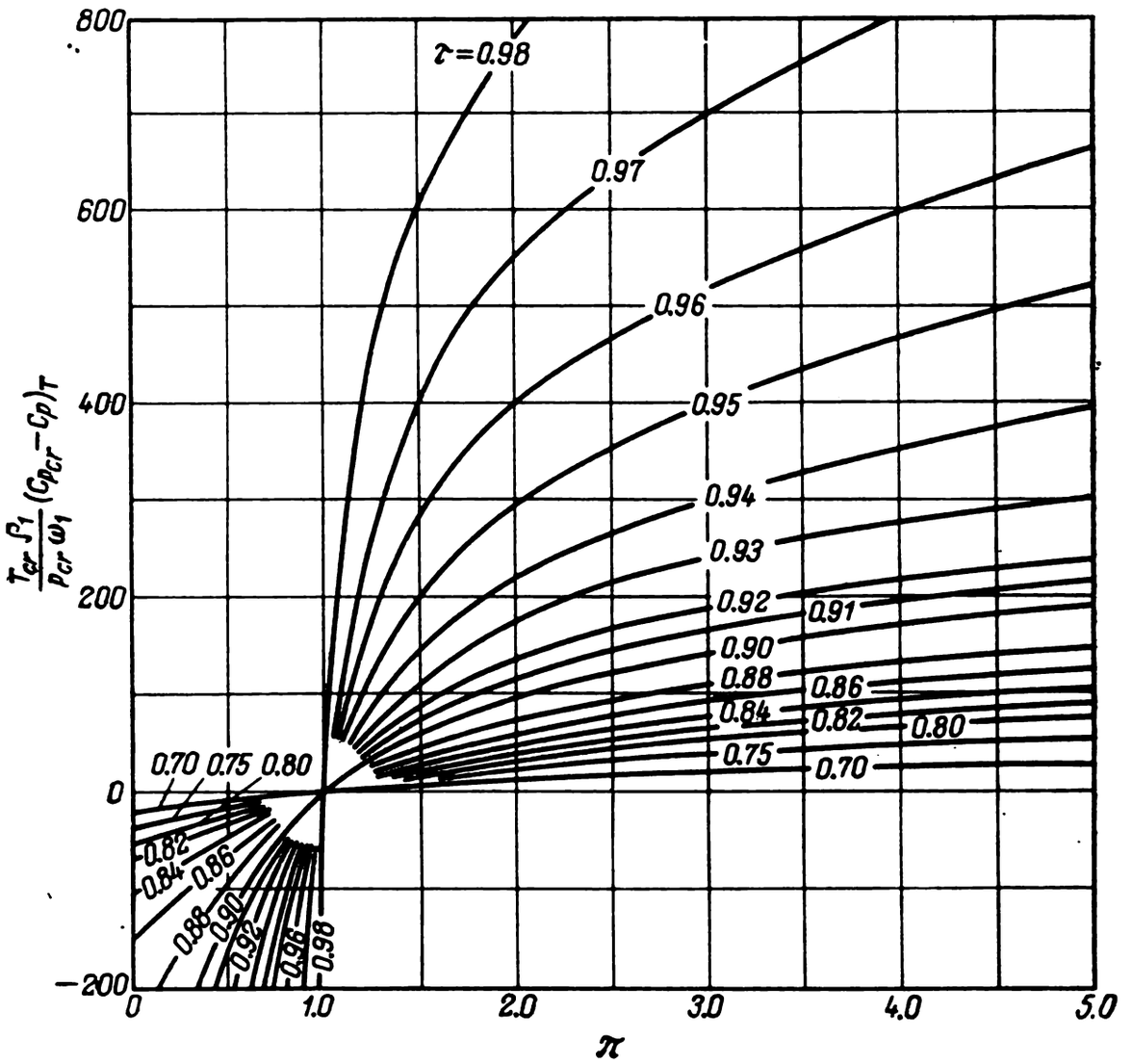

Fig. 48. Dependence of heat capacity of a liquid on the reduced pressure and temperature [C10]

The possibility of using the approximate universal equations to show the temperature dependence of a number of properties of a

liquid is illustrated for one example in Fig. 49, which gives the compression factor of a liquid related to the compression factor at the melting point as a function of $(T - T_m)/(T_{cr} - T_m)$.

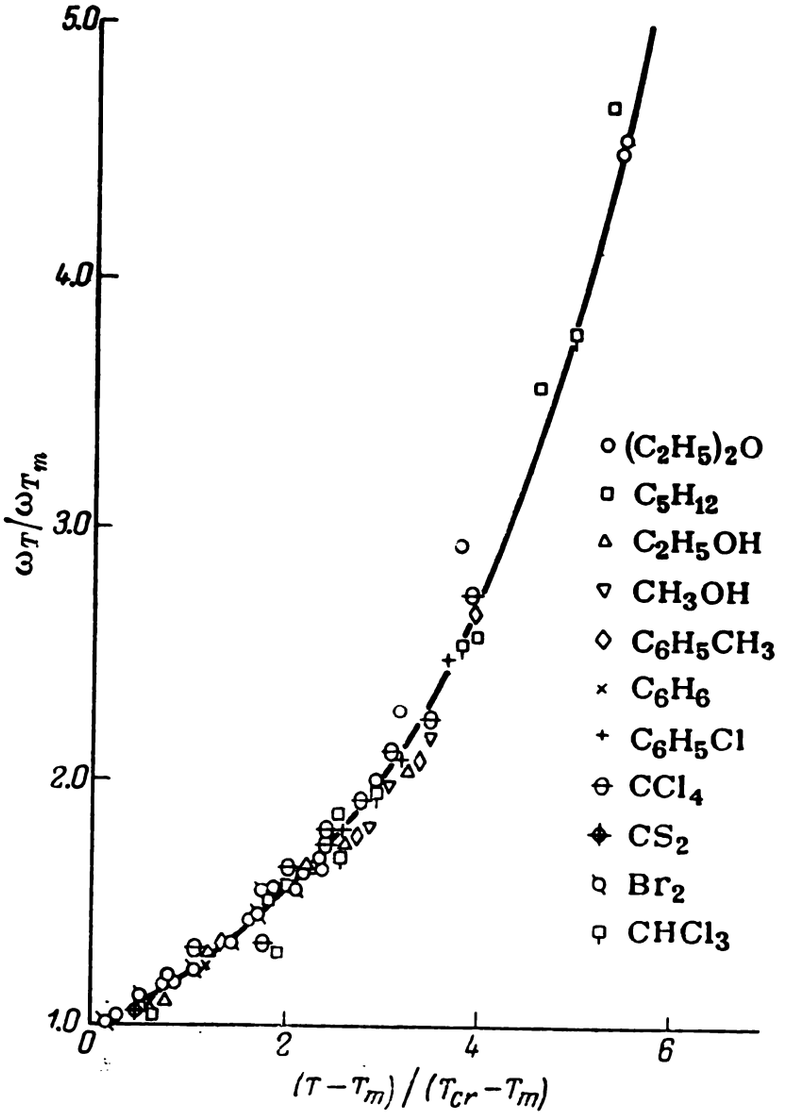

Fig. 49. Compressibility of selected liquids

Example 17. The density of water at $t = 150\,°C$ and $p = 50$ kgf/cm² equals 0.9194 g/cm³. Find (1) the critical volume and (2) the volume at $t = 300\,°C$ and $p = 250$ kgf/cm².

Solution. 1. $\tau_1 = 0.654$ and $\pi_1 = \frac{50/1.033}{218.5} = 0.222$ (1 atm = = 1.033 kgf/cm²). From Fig. 45 we have $\omega_1 = 0.120$, therefore

$$\frac{\rho_1}{\omega_1} = \frac{0.9194}{0.120} = 7.66$$

and

$$\rho_{cr} = 7.66 \times 0.044 = 0.3371 \text{ g/cm}^3$$

whence $V_{cr} = 2.97$ cm³/g, which differs from the tabulated value [D98] by 4%.

2. We have $\tau_1 = 0.885$ and $\pi_1 = 1.11$; from Fig. 45 we find $\omega_1 = 0.0955$. Hence $\rho = 7.66 \times 0.0955 = 0.732$ or $V = 1.367$ cm³/g, which differs from the tabulated value [D98] by 0.7%.

Chapter 7

ONE-COMPONENT HETEROGENEOUS SYSTEMS

7.1. RELATIONSHIP BETWEEN TEMPERATURE AND PRESSURE WITH COEXISTING PHASES

7.1.1. Clapeyron-Clausius Equation

As a result of the composition being constant, *in a one-component system the chemical potential is identical with the molar thermodynamic potential.* Therefore, when p and T are constant, the equality of the molar Gibbs energies of the coexisting phases is the condition for equilibrium.

Assume that in a two-phase equilibrium system the pressure changes isothermally. In accordance with Eq. (5.25), this will cause the Gibbs energy in the first phase to change by $V'dp$, and in the second by $V''dp$.* Since $V' \neq V''$, then $dG' \neq dG''$, i.e. equilibrium is violated. An isobaric change in the temperature also results in violation of equilibrium, because by Eq. (5.24) we have $dG' = -S'dT$ and $dG'' = -S''dT$, but $S' \neq S''$. For example, if we isothermally increase the pressure in an equilibrium system liquid-vapour, the vapour will condense ($V^g > V^{lq}$ and $dG^{lq} < dG^g$).** If isobaric heating is conducted, the liquid will evaporate [$S^g > S^{lq}$ and $dG^g < dG^{lq}$ (see also Chap. 5, Example 5, p. 140)]. A simultaneous change in both parameters makes it possible to maintain equilibrium, i.e. to continuously remain on the p-T-curve corresponding to the coexistence of both phases (Figs. 50*b* and 51).

Thus, to pass over from a given equilibrium state to another one, both p and T have to be changed simultaneously. This corresponds to the phase rule, since in accordance with Eq. (5.48), a two-phase one-component system has one degree of freedom; by indicating, for example, the temperature of a boiling liquid, we fix the pressure of its saturated vapour and all its properties.

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* We shall use the superscript ′ for the phase that is stable at a low temperature.

** The superscript "g" here and in the following denotes the saturated vapour, i.e. the vapour in equilibrium with the liquid (or crystalline) phase.

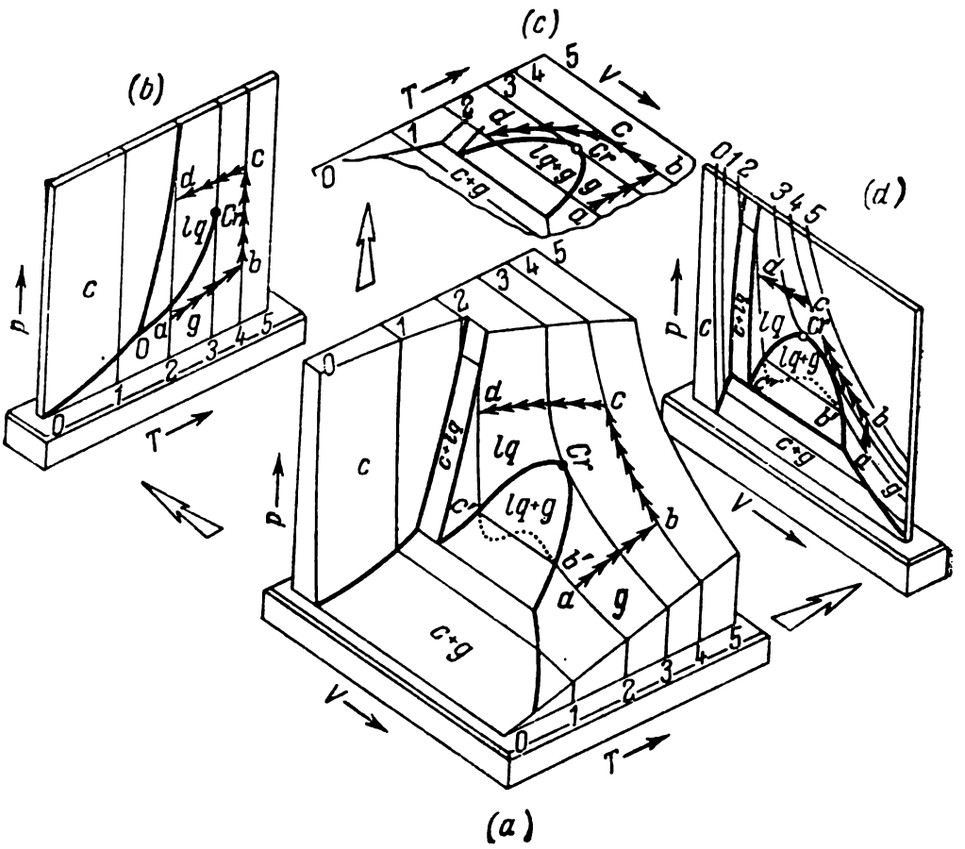

Fig. 50. Three-dimensional phase diagram (*a*) and its projections onto the plane *p*-*T* (*b*), *V*-*T* (*c*) and *p*-*V* (*d*)

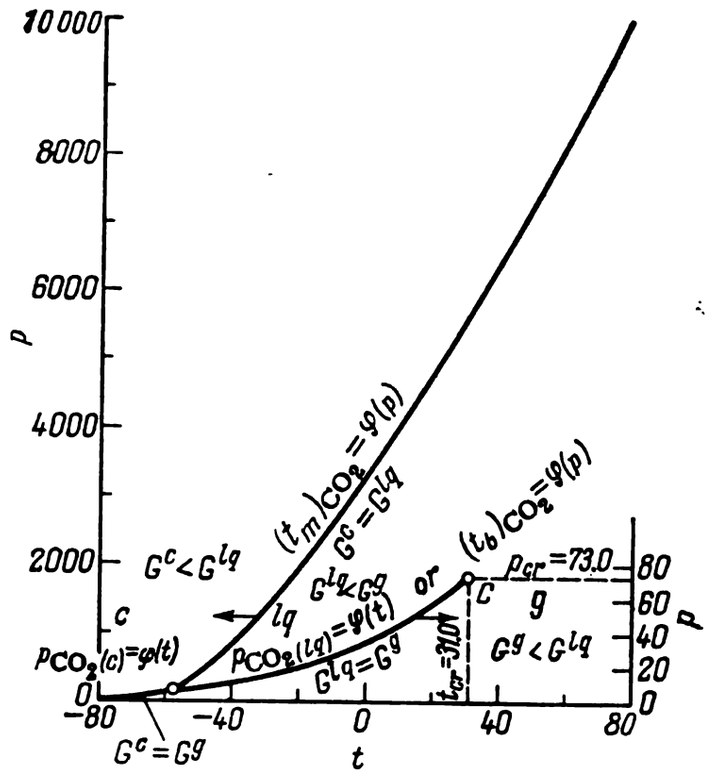

Fig. 51. Phase diagram for carbon dioxide

Consequently, the condition of equilibrium will be expressed by the equation

$$V' dp - S' dT = V'' dp - S'' dT$$

or

$$\left(\frac{\partial p}{\partial T}\right)_{eq} = \frac{S'' - S'}{V'' - V'}$$

where the subscript "eq" (which will be discarded in the following) shows that the derivative expresses the dependence of p on T on the curve of *coexistence* of two phases.

This equation can also be obtained directly from Eq. (6.18), since the subscript V in the right-hand side may be omitted (the pressure of the saturated vapour in accordance with the phase rule does not depend on the volume), and the derivative $(\partial S/\partial V)_T$ can be replaced by the ratio $\Delta S/\Delta V$ (in the system being considered, the increase of the mass of one phase at the expense of that of the other is the only conceivable process).

When p, $T = \text{const}$, the transition of the substance from one phase into the other in equilibrium with it is reversible. Hence, in accordance with Eq. (5.22), the relationship $p = \varphi(T)$ becomes

$$\frac{\partial p}{\partial T} = \frac{H'' - H'}{T(V'' - V')} = \frac{\Delta H}{T\Delta V} \tag{7.1}$$

where T and p = parameters of the equilibrium phase transition

ΔH = molar heat of phase transition (melting, vaporization, sublimation and the corresponding reverse processes, and also transitions from one crystalline modification to another)

ΔV = molar change in the volume upon a given transition.

When these quantities are expressed in the units of p, T and ΔH used in this book, calculations by means of the above equation should be performed after inserting the factor 41.293 (1 cal = $= 41.293$ atm·cm^3) into the numerator of its right-hand side.

Although ΔH is a characteristic of an irreversible process, its use in the above equation of a reversible process is natural, since $\Delta G = 0$ and by Eq. (5.22) we have $T\Delta S = \Delta H$. This explains the substitution of $\Delta H/T$ for ΔS used in deriving Eq. (7.1).

Equation (7.1) is called the **Clapeyron-Clausius equation** *. It is an equation of the curves $p = \varphi(T)$ corresponding to two-phase

* The equation introduced by B. Clapeyron (1834) contained an unknown function of the temperature. The equation was given its final form (7.1) by R. Clausius (1850) and W. Thomson (1850).

equilibria. Equation (7.1) also determines the position of the point of intersection of these curves (see Fig. 51), which corresponds to the equilibrium of three phases, i.e. the **triple point.** Only at this point is the equation $\Delta H_{subl} = \Delta H_f + \Delta H_{vap}$ absolutely accurate.

A comparison of the quantities in the right-hand side of Eq. (7.1) shows that the angular coefficients for the curves of vaporization and sublimation (somewhat greater for the second curve) are close in value. Since ΔV in melting (and polymorphic transformations) is insignificant, the angular coefficient is very great (the curve is almost vertical), the slope of the curve may be considered constant, although for a very great interval of pressures the change in the slope may become considerable (see Fig. 51).

In all the above cases, $(\partial p/\partial T) > 0$. The only exceptions are the p-T-curves for the processes of the melting of ice, bismuth, gallium, antimony, germanium, silicon and certain grades of iron, which have a negative angular coefficient. This explains one of the most important practical anomalies of water: the lowering of the melting point of ice with increasing pressure. This anomaly in accordance with the principle of displacement of equilibrium is due to compression in melting. It is observed only to about 2200 atm. Above this pressure ΔV changes its sign, because the ice transforms into a modification that is denser than water.* Research conducted by P. Bridgman and G. Tammann showed that ice exists in several forms (see Fig. 52).

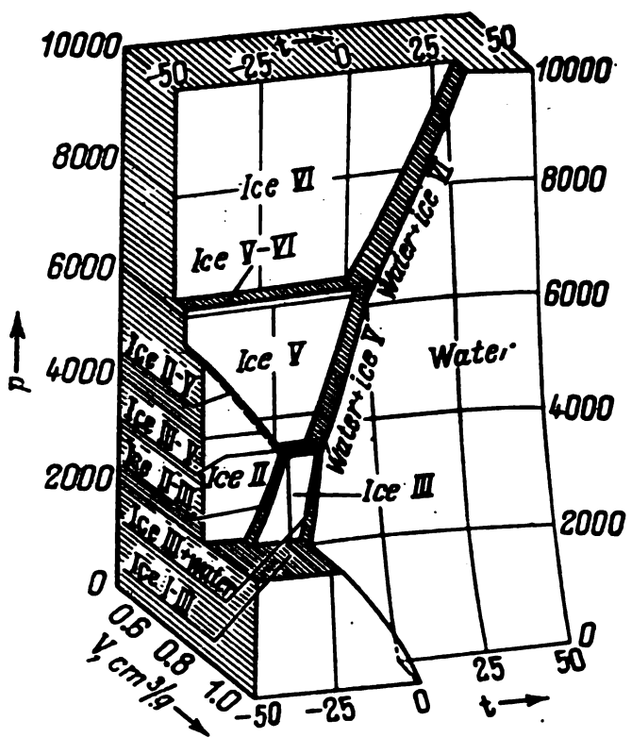

Fig. 52. Three-dimensional phase diagram for water

This anomaly at very high pressures is characteristic of the polymorphic transformations of many substances.

It is often very difficult to determine the heat of a phase transition. This is the reason why it is preferred to find the relationship $p = \varphi(T)$ experimentally, and then calculate ΔH by Eq. (7.1). The latter equation can also be used to calculate the volume of a vapour when its experimental determination becomes

* The experiment involving the regelation of ice, for instance, is based on this anomaly.

inaccurate because of its great rarefaction. Finally, Eq. (7.1) permits us to find the relationships $p = \varphi(T)$ and $T = \varphi(p)$.

Example 1. The pressure dependence of the melting point of alpha-naphthol is expressed by the equation $t_m = 96.0 + 248 \times \times 10^{-4} p - 65 \times 10^{-8} p^2$. Find (1) the change in t_m with a change in the pressure (when p changes by 1 atm) at the melting point at $p = 100$ atm; (2) t_m at $p = 100$ atm; and (3) the change in V in melting if $p = 100$ atm and $\Delta H_f = 39.0$ cal/g.

Solution. According to the above equation, we calculate:

1. $(\partial t_m/\partial p)_{p=100} = 0.024\,67$.
2. $(t_m)_{p=100} = 98.47$.
3. Using these values in Eq. (7.1), we get $1/0.024\,67 = (39.0 \times \times 144.2 \times 41.29)/371.7\,\Delta V$, whence $\Delta V = 1.541$.

7.1.2. Approximate Relationships

Equation (7.1), while being absolutely accurate, is not in great favour, since it contains four relationships [$p = \varphi(T)$, $\Delta H = \varphi(T)$, $V' = \varphi(T)$ and $V'' = \varphi(T)$], and to calculate one of them the other three must be known. This equation can be simplified, however, for regions of moderate vapour pressures.

If we ignore the volume of the condensed phase and assume that the Mendeleev-Clapeyron equation holds for a saturated vapour, then from Eq. (7.1) we obtain

$$\frac{\partial p}{\partial T} = \frac{\Delta H p}{RT^2} \text{ or } \frac{\partial \ln p}{\partial T} = \frac{\Delta H}{RT^2} \text{ or } \frac{\partial \ln p}{\partial T^{-1}} = -\frac{\Delta H}{R} \qquad (7.2)$$

In view of the assumptions made in deriving it, Eq. (7.2) may be used only for calculating processes of vaporization (condensation) and sublimation (desublimation).

In the following, we shall concentrate mainly on liquid-vapour equilibrium, which is encountered in practice most often. Sublimation, as a rule, occurs at very low pressures, with the exception of a few substances, for instance carbon, for which at the triple point we have $p \approx 100$ atm and $T \approx 4000$ K.

Within a narrow temperature interval, the derivative $\partial p/\partial T$ in Eqs. (7.1) and (7.2) may be replaced with the ratio $\Delta p/\Delta T$, which appreciably simplifies calculations.

Inspection of Fig. 53, which in three different scales gives the temperature dependence of saturated water vapour pressure, shows how narrowing of the temperature interval diminishes the curvature of the lines. The slope of curve *3* corresponding to a quite narrow temperature interval is virtually constant.

If the interval is great, the quantity $\partial p/\partial T$ can be found by graphical differentiation (see Fig. 53). The determination of $\partial p/\partial T$ from the graph makes it possible to find ΔH_{vap} or ΔH_{subl} by Eq. (7.2) for a given temperature (pressure).

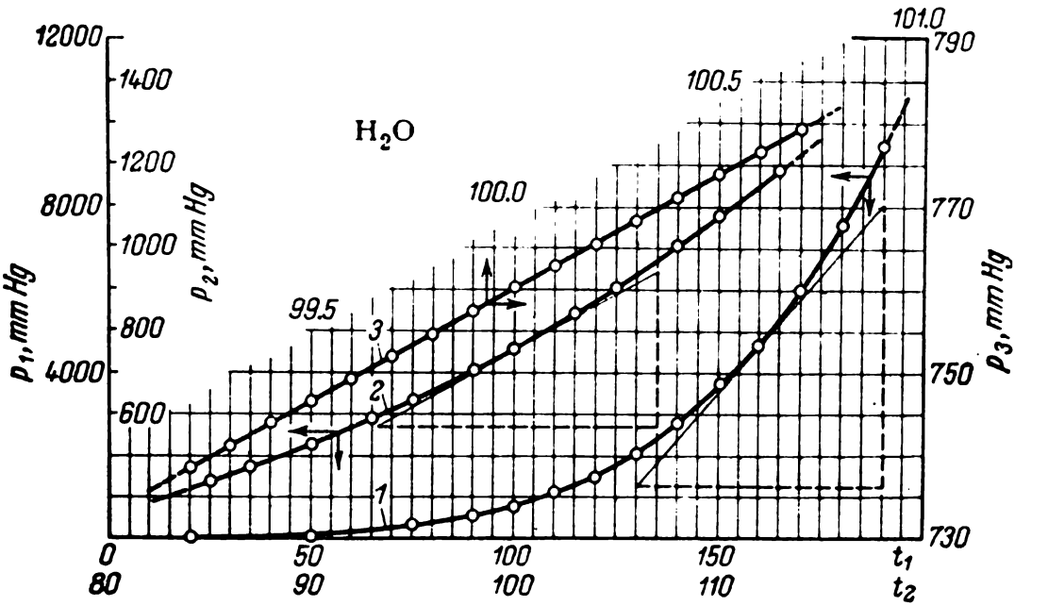

Fig. 53. Temperature dependence of saturated water vapour pressure.
(See Example 2)

If we assume in the first approximation that ΔH_{vap} (or ΔH_{subl}) is constant, then integration of Eq. (7.2) gives

$$\log p = -\frac{\Delta H_{vap}}{4.576T} + \text{const} \quad \text{or} \quad \log p = A - \frac{B}{t + 273.2} \tag{7.3}$$

Equation (7.3) permits us to assess the order of magnitude of the vapour pressure at practically any temperature, since a graph plotted in the coordinates $\log p$ against T^{-1} gives a straight line within a broad interval of temperatures * (Fig. 54). Hence it follows that notwithstanding the diminishing of ΔH_{vap} with increasing temperature (see Fig. 62, p. 234), the vapour pressure can be extrapolated according to the above graph, and also (which is the same) be calculated by Eq. (7.3) or the equation

$$\log \frac{p_2}{p_1} = \frac{\Delta H_{vap}}{4.576}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{7.4}$$

* Only near the critical point do the experimental points begin to deviate downward somewhat from the straight line. With small dimensions of the drawing, however, the coincidence of the points with the straight line may be deceptive, since a *logarithmic* scale is used on the axis of ordinates. Indeed, a difference, for instance, of 1 mm with a scale of 1 cm = 0.2 units of $\log p$ corresponds to an error in the value of the vapour pressure of 4.5%.

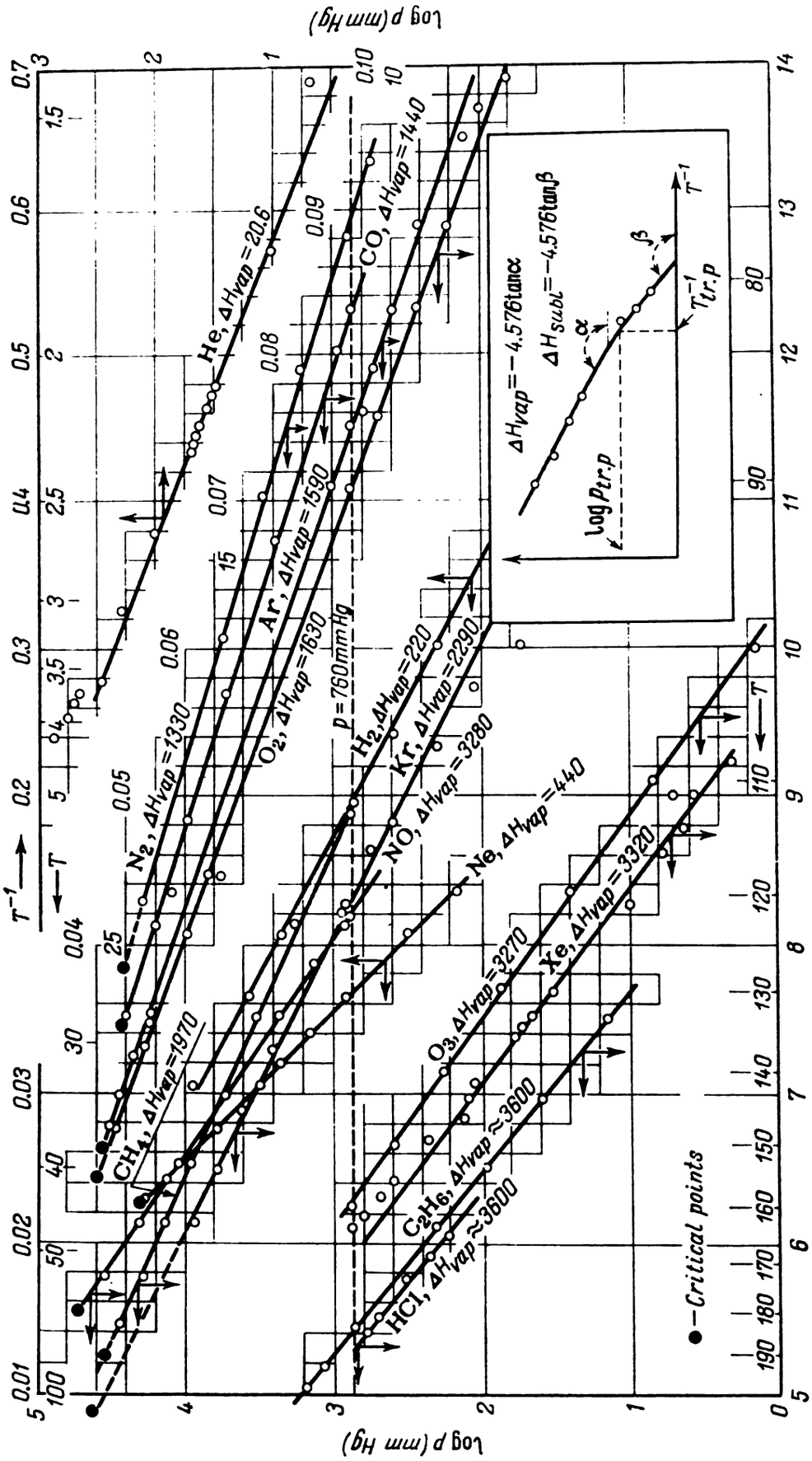

Fig. 54. Dependence of logarithm of saturated vapour pressure of selected liquids on the inverse absolute temperature. Verification of Eqs. (7.3) and (7.4)

Therefore, *in the general case,* neither a graph nor Eqs. (7.3) and (7.4) are suitable for the accurate calculation of ΔH_{vap}. In other words, we cannot indicate precisely the temperature which the value of ΔH_{vap} found by the equations or from the slope of the straight line $\log p = \varphi(T^{-1})$ (Fig. 54) relates to. The straightness of the line and thus the seeming constancy of ΔH_{vap} are a consequence of its actual decrease, because the diminishing of ΔH_{vap} with increasing temperature and the absence of a quantity characterizing the deviation of the behaviour of a vapour from that of an ideal gas approximately compensate our disregarding the volume of the liquid phase (since at high boiling points the pressure of a vapour only slightly differs from its fugacity, the decrease in ΔH_{vap} apparently has the main significance). For temperatures far from critical, the numerator and denominator of Eq. (7.2) are excessive by about the same amount; consequently the essentially incorrect assumptions only slightly affect the left-hand side of this equation. Therefore, the quantity ΔH_{vap} in Eqs. (7.2)-(7.4) may be considered as practically equal to $(\Delta H_{vap})_{n.b.p.}$ — the heat of vaporization at the normal boiling point (n.b.p.). The values of ΔH_{vap} indicated in Fig. 54 and calculated from the slope of the straight lines shown in the figure are close to $(\Delta H_{vap})_{n.b.p.}$. Owing to the assumptions made in deriving Eq. (7.4), however, the values of ΔH_{vap} calculated by this equation even for $p \leqslant 1$ atm somewhat exceed the calorimetrically found values.

A more accurate expression of the relationship $p = \varphi(T)$ for a broad temperature interval is obtained if instead of Eq. (7.3) we use equations of the kind

$$\log p = -\frac{A}{T} + B \log T + CT + \ldots + \text{const} \qquad (7.5)$$

The latter are obtained from Eq. (7.2) by expressing ΔH_{vap} as a function of temperature, and taking into account the errors connected with the transition from Eq. (7.1) to Eqs. (7.2) and (7.3). The result is the more accurate, the greater is the number of terms in Eq. (7.5). Usually, only three terms are used. The equation

$$\log p = -\frac{A}{T} + B \log T + C$$

gives the relationship being considered up to T_{cr} with an error generally not exceeding 3%, although a linear diminishing of ΔH_{vap} with the temperature up to T_{cr} is not observed (see Fig. 62, p. 234 and it is only the *formal* basis of the three-term equation (the p-T-relationships are also discussed in Secs. 13.6.3 and 15.2).

In conclusion we shall give Antoine's empirical (interpolation) equation

$$\log p = A - \frac{B}{C + t} \tag{7.6}$$

which is convenient not only for calculating $p = \varphi(T)$ and $\partial p/\partial T$, but also for finding $T = \varphi(p)$ and $\partial T/\partial p$. The maximum accuracy can be achieved by dividing the entire region of coexistence of a liquid and vapour into two or three parts and forming Eq. (7.6) for each of them.

A review of the methods of calculating the saturated vapour pressure for various inorganic and organic substances is contained in [B46].

Example 2. Use Fig. 53 to find (1) ΔH_{vap} for water at $p = 1$ atm and at a pressure corresponding to $t_b = 160\,°C$, and (2) the change in the boiling point of water with pressure at $t = 100\,°C$ (in kelvins per mm Hg).

Solution. 1. We draw in Fig. 53 a tangent to curve *2*; in accordance with Eq. (7.2) we get for $p = 1$ atm and $T = 373.2$ K

$$\frac{\partial p}{\partial T} = \frac{3.7 \times 100}{13.8} = \frac{\Delta H_{vap} \times 760}{1.987 \times 373.2^2}$$

whence $\Delta H_{vap} = 9790$ cal/mol or 543.8 cal/g.

Similarly from the slope of a tangent to curve *1* (at the point where $t = 160\,°C$ and $p = 4700$ mm Hg), we find

$$\Delta H_{vap} = 1.987 \times 433.2^2 \times 6.8 \times \frac{1000}{6.0 \times 10 \times 4700} =$$

$$= 8992 \text{ cal/mol or } 499.1 \text{ cal/g}$$

These results differ from experimental data [D97] by 0.9 and 0.4%, respectively.

2. Using line *3* (since it is drawn to an appropriate scale), we find

$$\frac{\partial T}{\partial p} \approx \frac{\Delta T}{\Delta p} = \frac{100.5 - 99.5}{774 - 746.5} = 0.0364 \text{ K/mm Hg}$$

Example 3. Using the method of mean values (see p. 70), find Eq. (7.3) for trichloroethene if investigation of the temperature dependence of its vapour pressure gave the following results:

t, °C	25.0	30.0	38.2	44.15	51.00	65.0	77.0	87.15
p, mm Hg ...	73	92	139	177	234	395	564	760

Solution. By converting the above data in accordance with Eq. (7.3) into $\log p$ and T^{-1}, we get:

$T^{-1} \times 10^6$ ...	3353	3298	3211	3152	3085	2957	2855	2775
$\log p$ (mm Hg)	1.8633	1.9638	2.1430	2.2480	2.3692	2.5966	2.7513	2.8808

Summing these values by groups of four gives $8.2181 = 4A + 0.013\,014B$ and $10.5979 = 4A + 0.011\,672B$, whence $A = 7.8238$ and $B = -1773$.

Therefore, the required equation has the form $\log p$ (mm Hg) $= 7.8238 - 1773/T$.

The mean error of the calculations according to the found equation equals 3.6%, which indicates the insufficient reliability of the experimental data on which the calculations are based.

Example 4. It was proposed to express the temperature dependence of the pressure for liquid argon by means of an equation of the kind (7.5) as follows:

$$\log p \text{ (mm Hg)} = -\frac{339.3}{T} + 1.75 \log T - 0.006\,737T + 3.9506$$

Find ΔH_{vap} for argon at $T = 87.5$ K.

Solution. By differentiating the equation $\log p = \varphi(T)$ with respect to T, in accordance with Eq. (7.2) we get

$$\frac{\partial \log p}{\partial T} = \frac{339.3}{T^2} + \frac{1.75}{2.303T} - 0.006\,737 = \frac{\Delta H_{vap}}{4.576T^2}$$

or

$$\Delta H_{vap} = 1552.3 + 3.477T - 0.030\,82T^2$$

whence $(\Delta H_{vap})_{87.5} = 1620$ cal/mol.

The approximate value found from the graph in Fig. 54 differs by 1.85%.

7.2. METHODS FOR THE COMPARATIVE CALCULATION OF THE TEMPERATURE DEPENDENCE OF THE SATURATED VAPOUR PRESSURE

The vapour pressure of various substances at the same temperature differs quite considerably, but all the curves of $p = \varphi(T)$ are of the same nature. Consequently, if a definite method of plotting the p-T-relationship for a substance results in a straight line, then this relationship will usually be linear for other substances. This under-

lies the methods of comparative calculations, in which the vapour pressure of a given substance is compared with that of the substance chosen for comparison (the **standard** or **reference** substance). Although the methods of calculation directly giving the absolute value of p are more accurate, they require more time to find the coefficients of the equation to be employed for calculations [of the type of Eq. (7.5)] and use it to determine $p = \varphi(T)$, let alone $T = \varphi(p)$. The methods of comparative calculations permit us to find the values of p with an accuracy sufficient for practical purposes with the aid of a minimum of initial data. The reliability of the results grows if a substance similar to the given one has been chosen as the standard substance, and if the relationship $p = \varphi(T)$ is known for it with a high degree of accuracy and within a broad interval of temperatures.

Below are treated several methods for the comparative calculation of the relationship between the temperature and pressure on the curve for boiling. All of them (except the first) are particular examples of an approximate linear relationship of the kind

$$X_2 \approx AX_1 + B$$

serving as an example of the fourth method of comparative calculations [B45]; it compares the boiling points (or saturated vapour pressures) of two substances (substance 1 is the standard one) in conventional or functional scales.

7.2.1. Straight Line Method

A logarithmic scale of pressures is plotted along the axis of ordinates, and then a straight line is drawn diagonally upward from left to right at an arbitrary angle. This line serves as an expression of the temperature dependence of the vapour pressure for the chosen standard substance. Water is usually selected as this substance (for very high temperatures mercury is chosen, and for low ones — a low-boiling hydrocarbon).

The relationship $p = \varphi(T)$ for the standard substance is used to lay off the temperature scale. If we now plot the relationship $p = \varphi(T)$ for other substances on the graph, then, as can be seen from Fig. 55, we get straight lines.

For substances of one group (hydrocarbons, alcohols, metals, etc.) the straight lines converge at approximately one point (Fig. 56). This permits us to plot a straight line for a substance of a given homologous series according to one experimental value. The chart should be constructed for one of the "middle" homologues; hence for the "extreme", i.e. for very high- and low-boiling homologues,

the increasing curvature of the straight lines at their ends (convexity toward the line for the standard substance) will be comparatively small.

Example 5. The vapour pressure of HI(lq) at 0 and at 50 °C is equal to 3.70 and 13.9 atm, respectively. Determine $t_{n.b.p.}$ and p for $t = 30$ and 100 °C.

Solution. After converting the pressures from atmospheres to mm Hg (1 atm = 760 mm Hg), we apply a piece of tracing paper to the graph of $p = \varphi(t)$ (see Fig. 55) and connect the points indicated above. The resulting straight line, which we extrapolate in both directions, gives us $t_{n.b.p.} = -37$ °C (for $p = 760$ mm Hg) and $p = 8.7$ and 35 atm, respectively. The experimentally found values are −35.5 °C, 8.65 and 37.0 atm.

7.2.2. Method of Comparing Boiling Points of Given and Standard Substances at Equal Vapour Pressures

Having written down Eq. (7.2) for two substances and divided one equation by the other, assuming the constancy of the ratio

$$\frac{(\Delta H_{vap})_1/T_1^2}{(\Delta H_{vap})_2/T_2^2}$$

we find after integration

$$T_2 = \frac{(\Delta H_{vap})_1/T_1^2}{(\Delta H_{vap})_2/T_2^2} T_1 + \text{const} = AT_1 + B \text{ (at } p_2 = p_1) \quad (7.7)$$

where A and B are individual constants.

Laying off t_1 along one of the axes and t_2 along the other, we get for $p_2 = p_1$, in accordance with Eq. (7.7), a straight line. Each of such lines relates the temperatures at which the given and the standard (1) substances have the same vapour pressure (Fig. 57). To use this graph, we must have a table or a graph of the vapour pressure of the standard substance (for convenience these data are given in the same figure).

Example 6. Construct a graph of $t = \varphi(t_{H_2O})$ at $p = p_{H_2O}$ for methyl aniline and determine the saturated vapour pressure at $t = 140$ °C and the boiling point at $p = 7.6$ mm Hg if the normal boiling point of methyl aniline is $t_{n.b.p.} = 195.7$ °C, and at 100 °C it has a vapour pressure of 31.5 mm Hg. According to tabulated data the boiling points of water at pressures of 760 and 31.5 mm Hg are 100 and 29.8 °C, respectively.

Solution. We put a piece of tracing paper on Fig. 57 and draw a straight line through the two points $t = 195.7$, $t_{H_2O} = 100$ and $t = 100$, $t_{H_2O} = 29.8$. We use this line to find that at $t = 140\,°C$

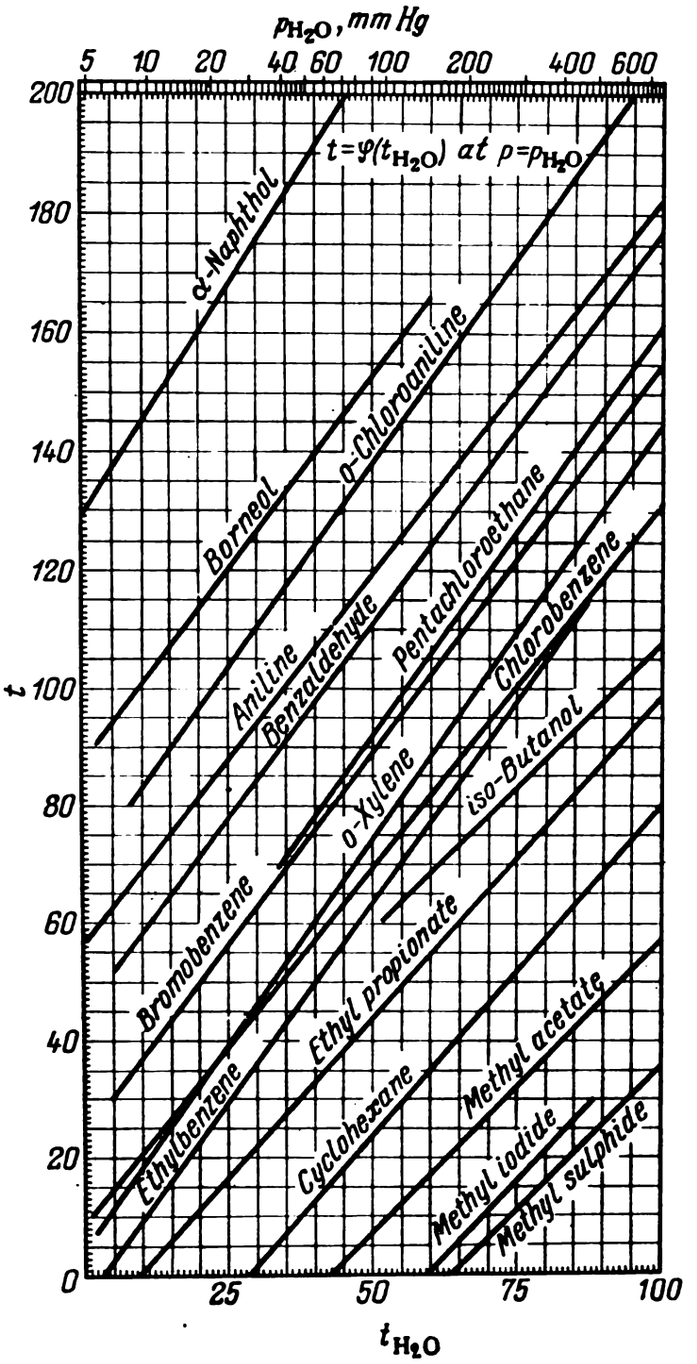

Fig. 57. Relationship between boiling points of water and selected liquids at equal pressure.
The graph is according to Eq. (7.7). (See Example 6)

the corresponding abscissa is $t_{H_2O} = 59.5\,°C$ and $p_{H_2O} = p = 146$ mm Hg. At $p = 7.6$ mm Hg, we have $t_{H_2O} = 7\,°C$ and $t = 68\,°C$.

The found values are close to experimental data — 147.6 mm Hg and 70 °C. The example can also be solved analytically by Eq. (7.7).

7.2.3. Method of Comparing Vapour Pressures of Various Substances at Equal Boiling Points

Having written down Eq. (7.2) for two substances and divided one equation by the other, assuming the constancy of the ratio $(\Delta H_{vap})_2/(\Delta H_{vap})_1$, we find after integration

$$\ln p_2 = \frac{(\Delta H_{vap})_2}{(\Delta H_{vap})_1} \ln p_1 + \text{const}$$

or

$$\log p_2 = A \log p_1 + B \text{ (at } t_2 = t_1) \qquad (7.8)$$

where A and B are individual constants.

A linear relationship $\log p_2 = \varphi(\log p_1)$ corresponds to this equation (Fig. 58). For convenience, the boiling points of the standard substance needed for the calculations are shown in the same figure. This method was proposed by V. Kireev (1931) and later by D. Othmer (1940); it is preferable to the preceding method, since its derivation is more precise, often more accurate and makes it possible to determine $(\Delta H_{vap})_2$ for a given substance by simply multiplying the slope of the straight line by $(\Delta H_{vap})_1$. Like the preceding one, however, this method is accurate only at temperatures far from critical: for high temperatures the ratio $(\Delta H_{vap})_2/(\Delta H_{vap})_1$ $\left[\text{or correspondingly } \frac{(\Delta H_{vap})_2/T_2^2}{(\Delta H_{vap})_1/T_1^2}\right]$ tends to zero or to infinity.

The Kireev-Othmer method can also be used for other purposes, in particular for calculating the vapour pressure over a solution. For this purpose, a graph can be used on which the vapour pressure of a standard substance (for example water) is laid off along the axis of abscissas, and the vapour pressure over the solution along the axis of ordinates. The straight lines will represent solutions having different concentrations.

Example 7. The temperature dependence of ΔH_{vap} for water is determined by the following data:

t	20	40	60	80	100
ΔH_{vap}	10 550	10 350	10 140	9925	9700

Calculate ΔH_{vap} for ethyl alcohol within the interval from 0 to 100 °C (through 20 kelvins) with the aid of Eq. (7.8). Take the data needed for the calculations from a reference book. Compare the results with experimental data ([D4], **7**: 331).

Solution. Placing a piece of tracing paper on Fig. 58, we use the relationship $p_w = \varphi(T)$ ([D4], **5**: 371) to plot the straight

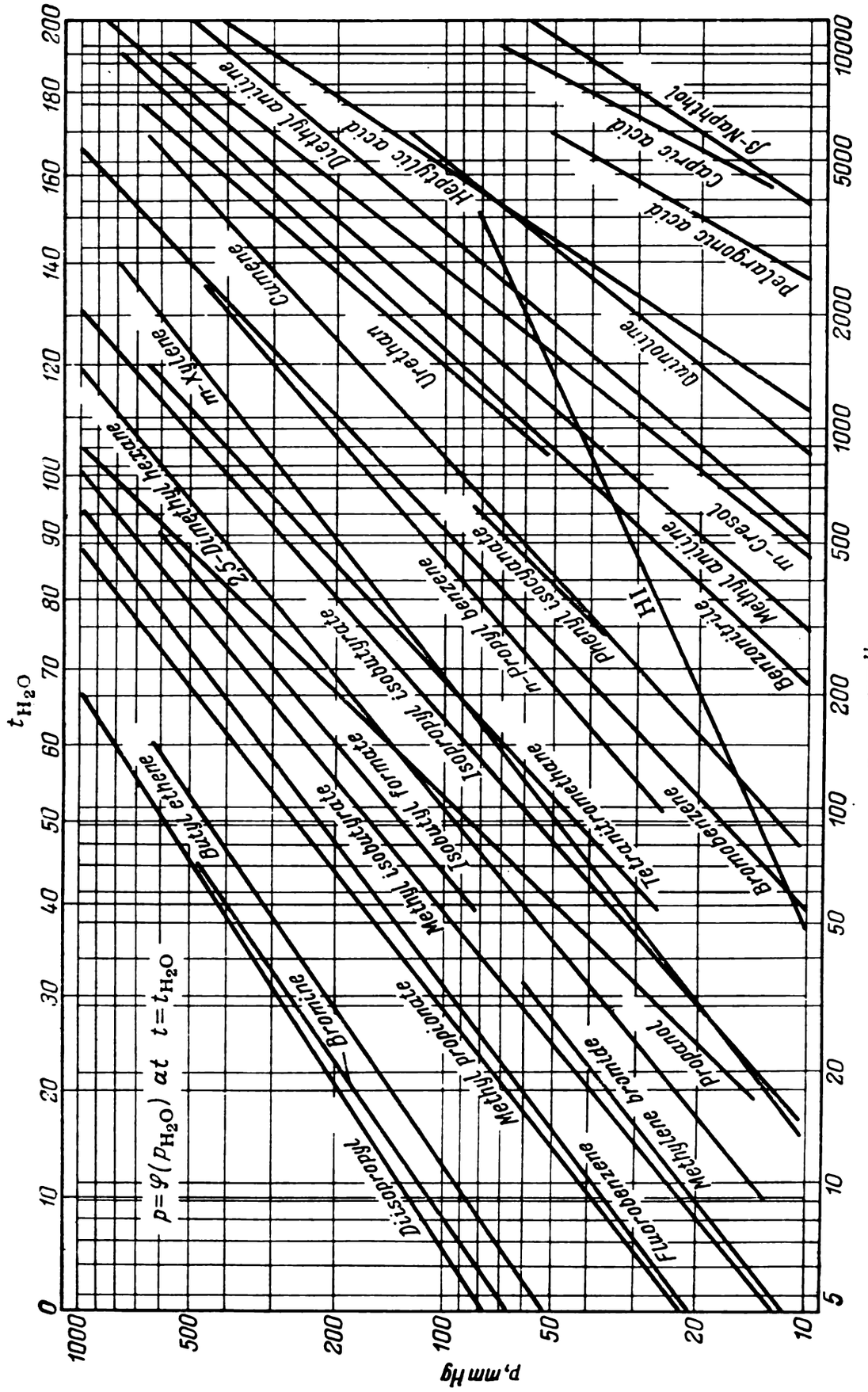

Fig. 58. Relationship between saturated vapour pressures of water and selected liquids at equal temperatures.
The graph is according to Eq. (7.8). (See Example 7)

line $\log p_{alc} = \varphi(\log p_w)$ whose slope relative to that of the line for water equals 0.97. (The subscripts "w" and "alc" stand for water and ethyl alcohol, respectively.) Multiplying $(\Delta H_{vap})_w$ by this quantity, we get the values of $(\Delta H_{vap})_{alc}$, which are given below together with the experimental data:

t	20	40	60	80	100
$(\Delta H_{vap})_{alc}$:					
calculated	10 230	10 040	9 840	9 630	9 410
experimental	10 010	9 910	9 680	9 350	9 080

The deviations of the calculated results from the experimental data are within the limits of the error of observations (the mean error is 2.1%).

7.2.4. Method of Comparing Vapour Pressures of Various Substances at Equal Reduced Boiling Points

The greater the difference between the critical temperatures of substances being compared (i.e. the greater these substances differ in their composition, structure and volatility), the lower is the temperature at which Eq. (7.8) becomes unsuitable.

We can, however, compare the vapour pressures not at equal temperatures, but at equal reduced temperatures, i.e. perform calculations according to the equation

$$\ln p_2 = \frac{(\Delta H_{vap})_2/(T_{cr})_2}{(\Delta H_{vap})_1/(T_{cr})_1} \ln p_1 + \text{const}$$

or

$$\log p_2 = A \log p_1 + B \quad (\text{at } \tau_1 = \tau_2) \tag{7.9}$$

where A and B are individual constants. We get comparatively accurate results up to the critical temperature. Figure 59 shows a graph plotted according to Eq. (7.9). Water was taken as the standard substance.

Example 8. Find the pressure of saturated ammonia vapour at $t = 31\,^{\circ}C$. To solve this problem, use Appendix 9, the relationship $p_w = \varphi(T)$ ([D4], **5** : 390) and the value of $p_{am} = 1.18$ at $t = -30\,^{\circ}C$ ("w" = water, "am" = ammonia).

Solution. We plot a graph in the coordinates $\log p_{am} = \varphi(\log p_w)$ for $(\tau_{am} = \tau_w)$ on which we mark two points: (1) $\tau \doteq (-30 + 273.2)/405.5 = 0.60$ and $p = 1.18$, and (2) $\tau = 1$ and $p = p_{cr} = 111.3$ (see Fig. 59). After connecting these points with a straight

line, we find by interpolation that the pressure at $\tau = (31+273.2)/405.5$ equals 11.8 atm. This value practically coincides with the experimental result (11.858 atm) ([D4], **5** : 391).

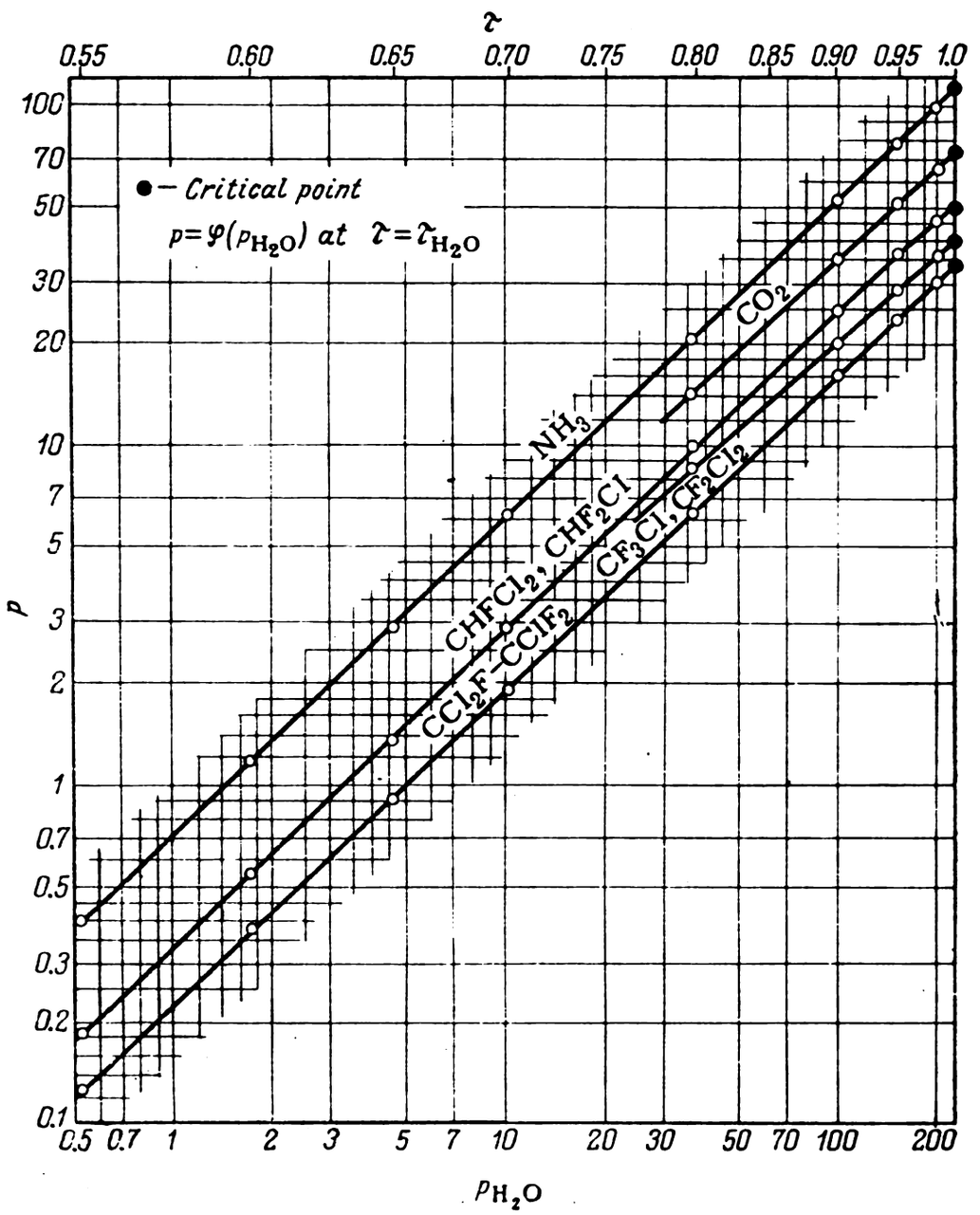

Fig. 59. Relationship between saturated vapour pressures of water and selected liquids.

The graph is according to Eq. (7.9). (See Example 8)

7.3. CRITICAL STATE

As we travel along the liquid-vapour equilibrium curve to the region of high temperatures and pressures, the difference between the properties of coexisting phases diminishes, and vanishes at the **critical point.**

The existence of such a temperature at which the difference between a liquid and its vapour disappears was indicated by D. Mendeleev (1860).

At the critical point (point *Cr* in Fig. 50, p. 206), the curve $p = \varphi(T)$ breaks off. This circumstance is confirmed by analysing Eq. (7.1). The introduction of the values $T = T_{cr}$, $H^g = H^{lq}$ and $V^g = V^{lq}$ into it transforms its right-hand side into indeterminacy, and this means breaking off of the curve.

In contrast to any other point on a liquid-vapour equilibrium curve, at the critical point *all* the thermodynamic properties of coexisting phases become identical. Since at this point an additional restriction is imposed on the system — identical properties of the liquid and vapour — the number of degrees of freedom at it is $f = 0$.

The region to the left of the isotherm $T = T_{cr}$ (see Fig. 51, p. 206) is sometimes said to correspond to the vaporous state, and to the right of it, to the gaseous state. Such a division, however, is neither urgent nor expedient. The terms "vapour" and "gas" may be considered essentially synonymous. A vapour, in contrast to a gas, condenses in isothermal compression, but this does not at all mean that their properties radically differ. Such an artificial division based not on the properties of a system, but on its behaviour in definite conditions has still another shortcoming. For example, it is hardly expedient to call carbon dioxide a vapour at $T < (T_{cr})_{CO_2}$, and water vapour or steam superheated to above $(T_{cr})_{H_2O}$, water gas. The term **superheated vapour** relating to the region under the curve $p = \varphi(T)$ cannot result in such misunderstandings, since it indicates the possibility of condensation of the vapour by isobaric cooling.

The existence of a temperature above which separation into the liquid and gaseous phases is impossible at any pressure, i.e. the two phases cannot coexist, is natural, since a liquid and a vapour at temperatures close to critical differ from each other only in a greater or smaller degree of interaction of their particles. It is therefore possible to carry out the continuous transformation of a liquid into a vapour and vice versa. For this purpose, the values of p and T should be selected so as to bypass the critical point, i.e. homogeneously pass over from the vapour to the liquid. This is shown in Figs. 50 (p. 206) and 60 (process *abcd*). When the state of a liquid changes along the path passing around the equilibrium curve, which confines the homogeneous region *ACrB*, the system will be homogeneous all the time, and it will be impossible to indicate the moment of transition from the vapour (white area) to the liquid (black area).

In contrast to the liquid phase, the crystalline and gas phases can coexist at high temperatures (and also below the triple point). A gas can transform into a crystal at $T > T_{cr}$, however, only at very

high pressures (see Fig. 51, p. 206), because the temperature interval between the triple and the critical points is great, while the melting curve has an exceedingly small slope. Therefore, if the transition of a vapour to the crystalline state occurs at $T > T_{cr}$, a modification of the crystalline substance may form that differs from the one

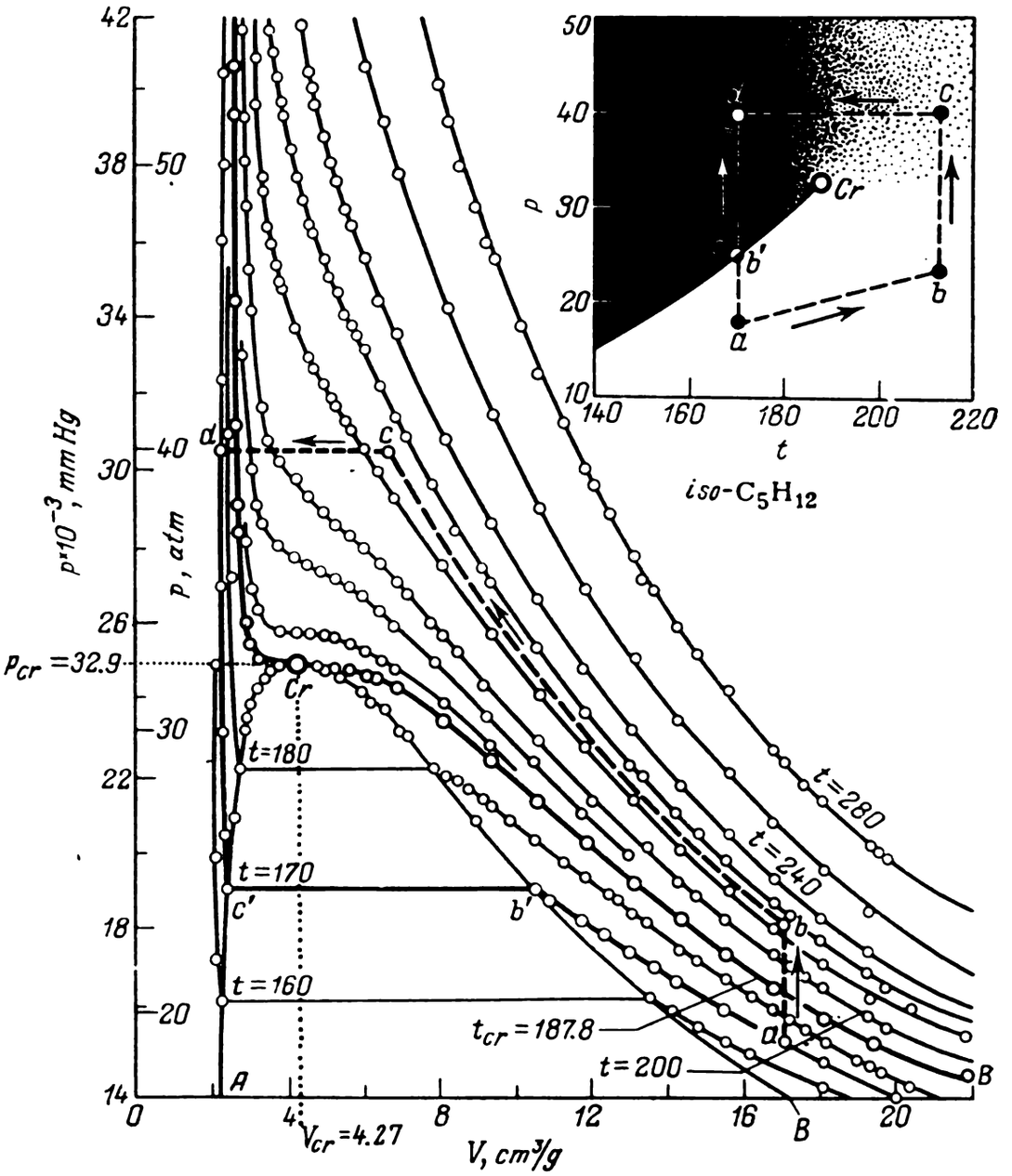

Fig. 60. Heterogeneous (*a-b'-c'-d*) and homogeneous (*a-b-c-d*) transitions from a vapour to a liquid.

(See Fig. 50*d*)

stable at a temperature below the temperature at the triple point. Another circumstance must also be taken into account: the very great growth in viscosity may result in such retarding of the processes causing crystallization (freezing) that no solidification will occur at the equilibrium pressure.

Critical Parameters. The coordinates of the critical point are determined by the equations

$$\left(\frac{\partial p}{\partial V}\right)_{T_{cr}} = 0 \tag{7.10}$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_{T_{cr}} = 0 \tag{7.11}$$

expressing the conditions of inflection of the critical isotherm (see Fig. 60). Consequently, the critical parameters can be calculated by the simultaneous solution of an equation of state true both for a liquid and a gas (for instance the van der Waals equation) and equations (7.10) and (7.11).*

The parameters p_{cr} and T_{cr} are simple to determine experimentally; one of these quantities can be found according to the other (analytically or graphically) if we know the relationship $p = \varphi(T)$ up to the critical point. Extensive numerical data on the critical temperatures were first obtained by M. Avenarius and his students — A. Nadezhdin, V. Zaionchevsky, etc. (1875-1887). Important works in the field of critical phenomena were written by A. Stoletov (1892, 1894).

The critical volume does not lend itself to accurate determination, since at $T = T_{cr}$ and $p = p_{cr}$ infinitely small changes in the pressure result in enormous changes in the volume. Indeed, from Eq. (7.10) it follows that $(\partial V/\partial p)_{T_{cr}} = -\infty$ i.e. the density of a substance at the critical point depends greatly on the pressure. The phenomenon of the fogging of a substance near the critical point ("critical opalescence") is due to violation of the homogeneity of a system as a result of fluctuation of the density. V. Semenchenko showed that such fluctuations of various properties are also observed at temperatures farther from critical. He also developed a theory based on the notion of phase transitions in the critical region as phase transitions of the second order (see Sec. 7.7).

Usually V_{cr} is determined on the basis of the **rule of the straight diameter:** if for a number of temperatures we compute the half-

* The reverse problem can also be solved, i.e. finding the constants of the equation of state a, b and c with the aid of the equation of state $\varphi(p, V, T, a, b, c) = 0$ and Eqs. (7.10) and (7.11). The equation of state becomes $\varphi(p, V, T, p_{cr}, V_{cr}, T_{cr}) = 0$, or, since p and p_{cr}, V and V_{cr}, and T and T_{cr}, respectively, have the same dimensions, then

$$\varphi\left(\frac{p}{p_{cr}}, \frac{V}{V_{cr}}, \frac{T}{T_{cr}}\right) = 0 \text{ or } \varphi(\pi, \delta, \tau) = 0$$

This proves the existence of a **reduced equation of state,** which is exactly what underlies the principle of corresponding states considered in treating the generalized method of calculating some properties of gases and liquids (see Sec. 6.6).

sum of ρ^g and ρ^{lq} and plot a graph of $1/2\ (\rho^{lq} + \rho^g) = \varphi(T)$, we get a straight line whose continuation to $T = T_{cr}$ gives the value of ρ_{cr} (Fig. 61). This approximate rule, as shown by A. Bachinsky, can be derived from Eq. (6.19).

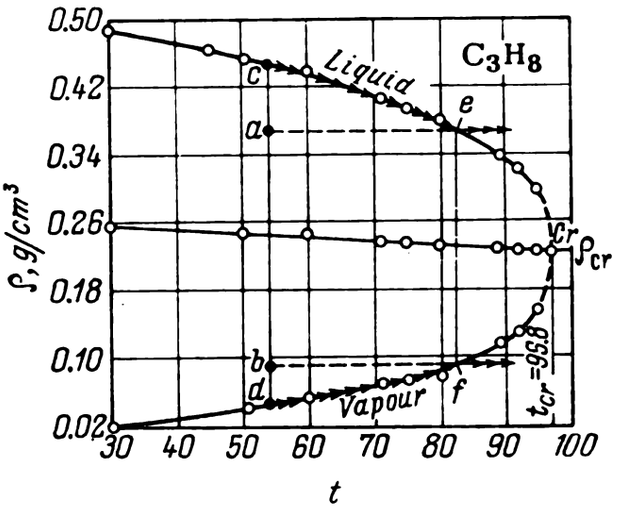

Fig. 61. Densities of a boiling liquid and its dry saturated vapour. (Rule of the straight diameter.)

(See Example 10)

A glance at Fig. 61 shows that if the volume of a mixture of a liquid and its saturated vapour (**moist,** or **wet** vapour) is less than the critical volume (point *a*), i.e. if $\rho > \rho_{cr}$, then upon *isochoric* heating of the mixture (line *ae*) complete condensation occurs (at point *e*). If $V > V_{cr}$ $(\rho < \rho_{cr})$, then isochoric heating (line *bf*) results in complete vaporization (at point *f*). In the first case, the mixture contains much liquid, and therefore the increase in its volume (along curve *ce*) exceeds the decrease in volume because of vaporization. As a result, the liquid-vapour interface rises, and in the long run the vessel will be filled with liquid. When the mixture contains much vapour, the tendency of vaporization predominates, and heating causes the **dryness fraction** of the vapour (i.e. its weight fraction in the mixture with the liquid) to grow. The interface will therefore move downward and at point *f* will reach the bottom of the vessel, i.e. the entire space will be occupied with dry saturated vapour. Only at $V = V_{cr}$ does homogenization set in when $t = t_{cr}$ $(p = p_{cr})$.

The ratio between the amount of vapour and liquid in each stage of the above process is determined by the **lever rule (rule of segments or rule of centres of gravity).** Thus, in a mixture corresponding to point *a* we have

$$\frac{\text{amount of liquid}}{\text{amount of vapour}} = \frac{ad}{ca}$$

This rule, which will be proved in Sec. 10.1, is widely used for drawing up material balances in various one- and multi-component heterogeneous systems (see Chaps. 9-11).

Hence, if the ratio between the mass of a liquid and the volume of the apparatus is less than the critical density, then vaporization sets in at $t < t_{cr}$. The relative amount of liquid is therefore of appreciable significance for the experimental determination of t_{cr} and p_{cr}.

The values of t_{cr} and p_{cr} for a number of substances are given in Appendix 9.

A number of empirical and semi-empirical equations have been recommended for calculating the critical parameters. Below we shall consider the method proposed by A. Lydersen (1955). He found the approximate relationships

$$\frac{T_{n.b.p.}}{T_{cr}} = 0.567 + \Sigma\Delta_T - (\Sigma\Delta_T)^2 \tag{7.12}$$

$$p_{cr} = \frac{M}{(\Sigma\Delta_p + 0.34)^2} \tag{7.13}$$

$$V_{cr} = 40 + \Sigma\Delta_V \tag{7.14}$$

where $\Sigma\Delta_T$, $\Sigma\Delta_p$ and $\Sigma\Delta_V$ are calculated by summing the additive components given in Table 8 *, and M is the molecular weight of a substance.

Example 9. Find the relationship between the critical parameters and the constants a, b and R from Eq. (6.19).

Solution. Combining Eqs. (7.10) and (7.11) with (6.19), we get

$$\frac{-RT_{cr}}{(V_{cr} - b)^2} + \frac{2a}{V_{cr}^3} = 0$$

and

$$\frac{2RT_{cr}}{(V_{cr} - b)^3} - \frac{6a}{V_{cr}} = 0$$

Simultaneous solution of these equations with Eq. (7.11) yields

$$p_{cr} = \frac{a}{27b^2} \quad \text{and} \quad T_{cr} = \frac{8a}{27Rb}$$

Using the values of p_{cr} and T_{cr} in Eq. (7.11), we find $V_{cr} = 3b$.

* The components for hydrogen are not taken into account.

Example 10. For propane $\rho^{lq} = 0.4858$ and $\rho^{g} = 0.0200$ at $t = 30\,°C$, and $\rho^{lq} = 0.3760$ and $\rho^{g} = 0.0832$ at $t = 80\,°C$. Calculate ρ_{cr} using the value of t_{cr} given in Appendix 9. Compare the result with Fig. 61.

Solution. According to the rule of the straight diameter we have $(\rho^{g} + \rho^{lq})/2 = \rho + Ct$, or for the data given in the initial conditions $0.2529 = \rho_{t=30} + 30C$ and $0.2296 = \rho_{t=80} + 80C$, whence $C = -0.000\,466$ and $\rho_{t=0} = 0.2669$. For the critical point, where $\rho^{g} = \rho^{lq} = \rho_{cr}$, the equation given above will become $\rho_{cr} = \rho_{t=0} + Ct_{cr}$, or $\rho_{cr} = 0.2669 - 0.000\,466 \times 96.8 = 0.2218$ and $V_{cr} = 4.51$ (according to experimental data 4.43).

Example 11. Use Eqs. (7.12)-(7.14) to determine the critical parameters of diethyl ether ($t_{n.b.p.} = 34.6\,°C$). Compare the results with the most reliable values given in Table 8.

Solution. In accordance with Eqs. (7.12)-(7.14) and the data indicated in Table 8, we find

$$\frac{307.8}{T_{cr}} = 0.567 + 2 \times 0.020 + 2 \times 0.020 + 0.021 = 0.668$$

$$p_{cr} = \frac{74.12}{(2 \times 0.227 + 2 \times 0.227 + 0.16 + 0.34)^2}$$

$$V_{cr} = 40 + 2 \times 55 + 2 \times 55 + 20$$

Hence $T_{cr} = 460.8$ K, $p_{cr} = 37.4$ atm and $V_{cr} = 280$ cm³, which differ from the most authentic values by 5.4 kelvins (1.2%), 1.8 atm (5.0%) and 0 cm³ (0.0%), respectively.

7.4. HEAT CAPACITIES OF COEXISTING PHASES AND HEATS OF PHASE TRANSITIONS

7.4.1. Heat Capacities of Coexisting Phases

The consumption of heat for heating one mole of a phase in equilibrium with another one (a boiling liquid, dry saturated vapour, a melting crystal, etc.) in accordance with Eq. (4.22) is determined by the quantity

$$\delta Q = T\,dS = C_{eq}\,dT \tag{7.15}$$

Since moving along the phase equilibrium curve is attended by a change in both p and T, the heat capacity of the corresponding equilibrium phase C_{eq} will differ from both C_p and C_V. Although for solids and liquids at temperatures sufficiently removed from the critical one, we have $C_{eq} \approx C_p$, in general both quantities may considerably differ from each other for dry saturated vapour.

Table 8. **Components Δ_T, Δ_p and Δ_V for Calculating the Critical Parameters by Eqs. (7.12), (7.13) and (7.14)***

Atoms, groups, bonds	Δ_T	Δ_p	Δ_V	Atoms, groups, bonds	Δ_T	Δ_p	Δ_V
B	(0.03)	—	—	$-\overset{\vert}{C}=O$	0.040	0.29	60
Br	0.010	(0.50)	(70)				
				$-\overset{\vert}{C}=O$ (in ring)	(0.033)	(0.2)	(50)
$-\overset{\vert}{\underset{\vert}{C}}-$	0.00	0.210	41				
				$HC\overset{\vert}{=}O$ (aldehydes)	0.048	(0.33)	73
				$-COOH$ (acids)	0.085	(0.4)	80
$-\overset{\vert}{\underset{\vert}{C}}-$ (in ring)	(−0.007)	(0.154)	(31)	$-COO-$ (esters)	0.047	0.47	80
				Cl	0.017	0.320	49
				F	0.018	0.224	18
				I	0.012	(0.83)	(95)
$=\overset{\vert}{C}-$	0.0	0.198	36	$-\overset{\vert}{N}-$	0.014	0.17	(42)
$=\overset{\vert}{C}-$ (in ring)	0.011	0.154	36	$-\overset{\vert}{N}-$ (in ring)	(0.007)	(0.13)	(32)
$=C=$	0.0	0.198	36	$-\overset{\vert}{N}H$	0.031	0.135	(37)
$=C=$ (in ring)	0.011	0.154	36				
$\equiv C-$	0.005	0.153	(36)				
				$-\overset{\vert}{N}H$ (in ring)	(0.024)	(0.09)	(27)
				$-NH_2$	0.031	0.095	28
$-\overset{\vert}{C}H$	0.012	0.210	51	NO_2	(0.055)	(0.42)	(78)

$-\overset{\vert}{\underset{\vert}{CH}}-$	(in ring)	0.012	0.192	46	$-O-$		0.021	0.16	20
					$-O-$	(in ring)	(0.014)	(0.12)	(8)
$=\overset{\vert}{CH}-$		0.018	0.198	45	$-OH$	(alcohols)	0.082	0.06	(18)
$=\overset{\vert}{CH}-$	(in ring)	0.011	0.154	37	$-OH$	(phenols)	0.031	(−0.02)	(3)
$\equiv CH$		0.005	0.153	(36)	$=O$	(except for cases indicated above)	(0.02)	(0.12)	(11)
$-CH_2-$		0.020	0.227	55	$-S-$		0.015	0.27	55
$-CH_2-$	(in ring)	0.013	0.184	44.5	$-S-$	(in ring)	(0.008)	(0.24)	(45)
$=CH_2$		0.018	0.198	45	$=S$		(0.003)	(0.24)	(47)
$-CH_3$		0.020	0.227	55	$-SH$		0.015	0.27	55
$-CN$		(0.060)	(0.36)	(80)	$-\overset{\vert}{\underset{\vert}{Si}}-$		0.03	0.54	—

* The atoms and groups are joined by the indicated bonds to non-homogeneous atoms. The values in parentheses have been found according to a limited number of data. The cyclic component $\overset{\vert}{\underset{\vert}{C}}-H$ common for two saturated rings has the value $\Delta_T = 0.064$.

Consider an infinitely small movement along the equilibrium curve of two phases (for example along curve OCr in Fig. 50*b*, p. 206). To determine C_{eq}, as follows from Eq. (7.15), we must find the change in the entropy in this process. By Eqs. (4.19) and (4.21), it will equal

$$dS = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_p dp \tag{7.16}$$

whence in connection with Eq. (7.15)

$$\delta Q = C_{eq}\, dT = C_p\, dT - T\left(\frac{\partial V}{\partial T}\right)_p dp \tag{7.17}$$

consequently

$$C_{eq} = C_p - T\left(\frac{\partial V}{\partial T}\right)_p \frac{\partial p}{\partial T} \tag{7.18}$$

or by Eq. (7.1)

$$C_{eq} = C_p - \left(\frac{\partial V}{\partial T}\right)_p \frac{\Delta H}{\Delta V} \tag{7.19}$$

Another accurate equation relating the values of the heat capacities of coexisting phases can be used for calculations. It is derived as follows. On one hand, Eq. (1.11) holds for a phase transition, whence

$$\frac{\partial \Delta H}{\partial T} = \frac{\partial \Delta U}{\partial T} + p \frac{\partial \Delta V}{\partial T} + \Delta V \frac{\partial p}{\partial T}$$

or by Eq. (7.1)

$$\frac{\partial \Delta H}{\partial T} = \frac{\partial \Delta U}{\partial T} + p \frac{\partial \Delta V}{\partial T} + \frac{\Delta H}{T} \tag{7.20}$$

On the other hand,

$$C''_{eq} - C'_{eq} = \left(\frac{\partial U''}{\partial T} + p \frac{\partial V''}{\partial T}\right) - \left(\frac{\partial U'}{\partial T} + p \frac{\partial V'}{\partial T}\right) = \\ = \frac{\partial \Delta U}{\partial T} + p \frac{\partial \Delta V}{\partial T} \tag{7.21}$$

Combining Eqs. (7.20) and (7.21), we finally obtain

$$C''_{eq} - C'_{eq} = \frac{\partial \Delta H}{\partial T} - \frac{\Delta H}{T} \tag{7.22}$$

Since the derivative $(\partial V/\partial T)_p$ is not great for solids and liquids, we can assume for them, as noted above, that $C_{eq} \approx C_p$. This also

follows from Eq. (7.18). Only near T_{cr} does the difference between C_{eq}^{lq} and C_p^{lq} become appreciable.

For a dry saturated vapour in equilibrium with a boiling liquid, Eqs. (7.19) and (7.22) can be replaced with the approximate relationships

$$C_{eq}^{g} = C_p^{g} - \frac{\Delta H_{vap}}{T} \tag{7.23}$$

and

$$C_{eq}^{g} = C_p^{lq} + \frac{\partial \Delta H_{vap}}{\partial T} - \frac{\Delta H_{vap}}{T} \tag{7.24}$$

It follows from Eqs. (7.18), (7.19) and (7.22)-(7.24) that C_{eq}^{g} may not only considerably differ from C_p^{g}, but also be a negative quantity. This conclusion seems unusual, because we are accustomed to work with values of C_p and C_V which according to their physical meaning cannot be less than zero.

To explain this paradoxical conclusion, we shall consider the transition of a phase from one equilibrium state to another infinitely close to it by heating. This "two-stage" transition is attended by the consumption of heat $\delta Q_p = C_p\, dT$ for superheating the vapour with the following isothermal compression leading back to the equilibrium curve, which involves the removal of the heat $\delta Q_T = T(\partial V/\partial T)_p\, dp$ [see Eq. (7.17)]. The sign of $\delta Q = \delta Q_p + \delta Q_T$, and therefore the sign of C_{eq}^{g}, is determined by which of the two quantities is greater — the first or the second. The quantities δQ_p and δQ_T and their ratio change along the equilibrium curve. At a certain temperature, C_{eq}^{g} may change its sign. This temperature is called the **inversion temperature.** At the inversion point, the curve $p = \varphi(T)$ for coexisting phases coincides with an adiabat. The inversion temperature naturally has a physical meaning only when it is higher than the triple point and lower than the critical one. Among the substances for which $C_{eq}^{g} < 0$ are H_2O, NH_3, CO, O_2 and many others.

It follows from the above reasoning that if a dry saturated vapour is subjected to adiabatic compression (strictly speaking, to *infinitely small* compression) in the region where $C_{eq}^{g} > 0$, it will condense, and upon adiabatic expansion it will become superheated. If $C_{eq}^{g} < 0$, then in adiabatic expansion the dry saturated vapour will condense, and in adiabatic compression it will become superheated. Finally, if $C_{eq}^{g} = 0$, then no matter whether a vapour is adiabatically expanded or compressed, it will remain saturated.

The negative value of the heat capacity of water vapour (this property makes it possible to observe the path of charged particles in a Wilson chamber) is of great importance for heat engineering.

Numerous theoretical and experimental investigations of the heat capacities of saturated vapours were conducted by N. Kolosovsky and his assistants.

Example 12. 1. Find C^g_{eq} for H_2O at 50 and 100 °C if

$$\Delta H_{vap} = 13\,425 - 9.81T + 0.075 \times 10^{-3}T + 0.466 \times 10^{-6}T^3$$

2. Compare the results with those calculated with the aid of water property tables (for example [D97]).

Solution. 1. Differentiation of the equation $\Delta H_{vap} = \varphi(T)$ with respect to T gives $\partial \Delta H_{vap}/\partial T = \varphi(T)$. Next by means of these two equations, we calculate the values of $\Delta H_{vap}/T$ and $\partial \Delta H_{vap}/\partial T$ for the indicated temperatures. We take the quantity $(C_p)^{lq}_{H_2O}$ equal to 18.0 cal/mol·K. Introducing these values into Eq. (7.24), we get

$$(C^g_{eq})_{t=50} = 18 - 9.6 - 31.8 = -23.4$$

$$(C^g_{eq})_{t=100} = 18 - 9.6 - 26.2 = -17.8$$

2. Assuming that

$$\frac{\partial \Delta H_{vap}}{\partial T} \approx \frac{\Delta H_{t_2} - \Delta H_{t_1}}{t_2 - t_1}$$

we get from water property tables [D97]:

for $t = 50$ °C

$$\frac{\partial \Delta H_{vap}}{\partial T} = \frac{18(568.4 - 569.5)}{51 - 49} = -9.9$$

$$\frac{\Delta H_{vap}}{T} = \frac{18 \times 569.0}{323.2} = 31.7$$

$$C^g_{eq} = 18 - 9.9 - 31.7 = -23.6$$

for $t = 100$ °C

$$\frac{\partial \Delta H_{vap}}{\partial T} = \frac{18(538.3 - 539.5)}{101 - 99} = -10.8$$

$$\frac{\Delta H_{vap}}{T} = \frac{18 \times 538.9}{373.2} = 26.0$$

$$C^g_{eq} = 18 - 10.8 - 26.0 = -18.8$$

7.4.2. Heats of Phase Transitions

At first sight, it seems that the temperature dependence of the heats of phase transitions can be found by Eq. (3.26). Strictly speaking, however, it cannot be used for the relationship being consid-

ered: in contrast to chemical reactions, physical transformations cannot proceed at different temperatures and a constant pressure (volume).

Accurate calculations can be performed with the aid of Eq. (7.1), while if the values of the equilibrium heat capacities are known, with the aid of Eqs. (7.19) and (7.22). In addition, we can use the equation

$$\frac{\partial \Delta H}{\partial T} = \Delta C_p + \left(\frac{\partial \Delta H}{\partial p}\right)_T \frac{\partial p}{\partial T} \tag{7.25}$$

which is obtained by combining the relationship

$$d\Delta H = \left(\frac{\partial \Delta H}{\partial T}\right)_p dT + \left(\frac{\partial \Delta H}{\partial p}\right)_T dp$$

with Eq. (3.26), or the equation

$$\frac{\partial \Delta H}{\partial T} = \Delta C_p + \frac{\Delta H}{T}\left[1 - \frac{T}{\Delta V}\left(\frac{\partial \Delta V}{\partial T}\right)_p\right] \tag{7.26}$$

obtained from Eqs. (7.25), (4.23) and (7.1).

It can be seen from Eqs. (7.25) and (7.26) that the Kirchhoff equation (3.26) cannot be used for accurate calculation of the temperature dependence of the heats of phase transitions. Owing to the absence of the relevant data, however, it is difficult to use all the above equations for calculating the heats of phase transitions. This is why Eqs. (7.25) and (7.26) are not widely used. They can be simplified somewhat without any great harm to their accuracy. For melting and a transition from one solid phase to another, the quantity $(\partial \Delta V/\partial T)_p$ is not great; by ignoring it, from Eq. (7.26) we get

$$\frac{\partial \Delta H}{\partial T} \approx \Delta C_p + \frac{\Delta H}{T} \tag{7.27}$$

Since for melting and allotropic transformations, the values of ΔC_p and $\Delta H/T$ are not great, the heat of these processes changes very slightly with the temperature. It should be noted that in experiments with H_2O, C_2H_5OH and C_4H_9OH conducted at very high pressures it was discovered that ΔH_f grows faster than T_m. Consequently, ΔS_m increases with the pressure, which again indicates the absence of a critical point on the melting curve.

For vaporization (and sublimation), neglecting the volume of the liquid (and crystalline body) and considering the vapour to be an ideal gas, we find

$$\frac{\partial \Delta H}{\partial T} \approx \Delta C_p \tag{7.28}$$

Although Eq. (7.28) gives exaggerated results, it is sufficiently simple and accurate for approximate calculations provided that the temperature is far from critical. It can be seen directly from Eq. (7.28) that the heat of vaporization diminishes with increasing temperature. Thus, for water $C_p^{lq} \approx 18$; assuming that $C_p^g \approx 14$, i.e. considering water vapour to be an ideal triatomic gas ($C_p^g \approx C_V^g + R = 3 + 3 + 6 + 2$), we get $\partial \Delta H_{vap}/\partial T \approx -4$ (actually, this derivative will be greater in its absolute value, since the assumed value of C_p^g is exaggerated).

Other methods of calculation also exist, the greatest attention being given to calculations of the heat of vaporization. It should be noted that few data are available on the temperature dependence of ΔH_{vap} and their average error is several per cent, whereas the order of magnitude of the error for the relationship $p = \varphi(T)$ is quite often only tenths and even hundredths of a per cent.

Heat and Entropy of Vaporization. If the heat of vaporization changes only slightly near the normal boiling point, then the closer the temperature approaches T_{cr}, the more appreciably does it diminish, this reduction being quite considerable near T_{cr} (Fig. 62).

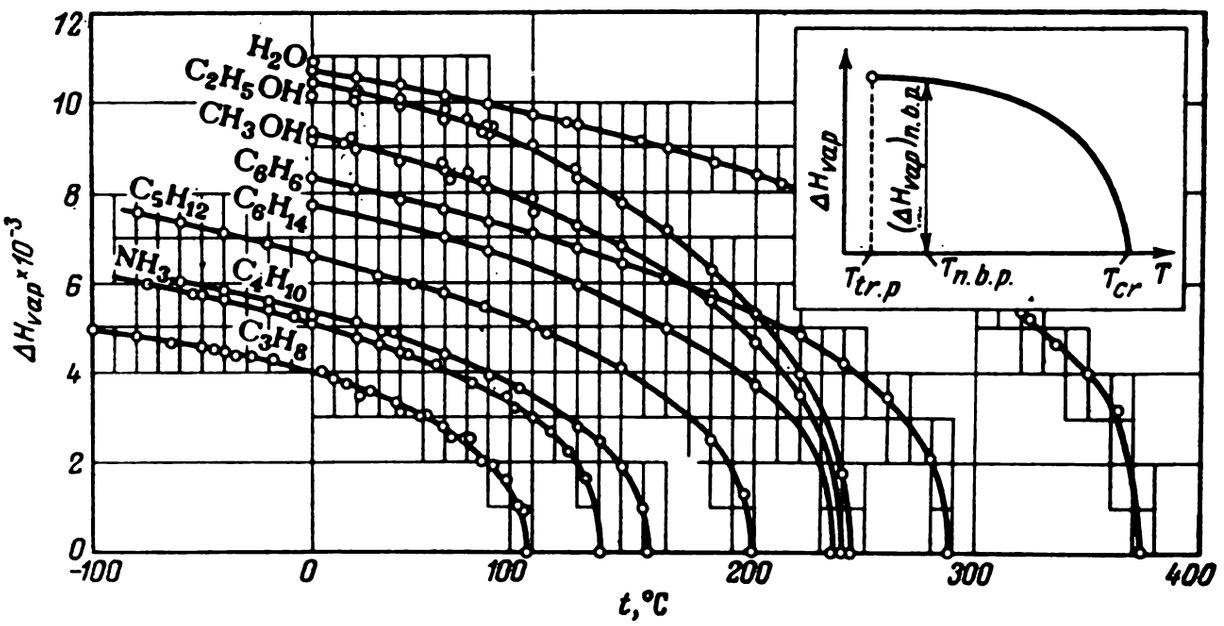

Fig. 62. Temperature dependence of heat of vaporization for selected liquids

The diminishing of ΔH_{vap} with increasing temperature does not contradict Eq. (7.1) — although $\partial p/\partial T$ grows with the temperature, the difference $(V^g - V^{lq})$ diminishes at a greater rate in this case.

In addition to the equations for calculating ΔH_{vap} considered in this section, equations (7.1)-(7.6) and (7.7)-(7.9) or their corresponding graphs (see Figs. 57-59) can also be used.

To introduce greater accuracy into the values of ΔH_{vap} calculated by Eq. (7.4), the author has proposed the following equation for use within the interval of $\pi = 0.001$ to 0.05:

$$\Delta H'_{vap} \approx \frac{\Delta H_{vap}}{1.008 + 1.4\pi} \tag{7.29}$$

where $\Delta H'_{vap}$ is the more accurate value of the heat of vaporization.

The quantity ΔH_{vap} can also be calculated with the aid of an equation of the form

$$\Delta H_{vap} = A + BT + CT^2 + \ldots$$

compiled similar to Eq. (3.29) by expressing the temperature dependence of $(C_p^g - C_p^{lq})$ and which is therefore empirical.

Many equations proposed for calculating $\Delta H_{vap} = \varphi(T)$ are accurate within a narrow temperature interval. Others, being comparatively accurate within a broad interval, are not convenient, since they contain several constants, among which there may be various thermodynamic parameters (p, V^g, V^{lq}, etc.), and require additional information and calculations.

In conclusion, we shall consider three more methods of calculation.

Combining Eqs. (4.6) and (7.18), we get a temperature dependence of the heat of a phase transition, which for vaporization can be represented by the equation

$$T \frac{\partial}{\partial T}\left(\frac{\Delta H_{vap}}{T}\right) = T \frac{\partial}{\partial T} \Delta S_{vap} = \Delta C_{eq} = C_{eq}^g - C_{eq}^{lq} \tag{7.30}$$

If Eq. (7.30) is accurate, its integration inevitably involves an error, because the relationship $\Delta C_{eq} = \varphi(T)$ must be established. Since $\Delta C_{eq} \neq 0$, by assuming consecutively that $\Delta C_{eq} = \text{const}$, $\Delta C_{eq} = A + BT$, etc., we find respectively from Eq. (7.20) that

$$\Delta S_{vap} = \Delta C_{eq} \ln T + \text{const} = A \ln T + B \tag{7.31}$$

$$\Delta S_{vap} = A \ln T + BT + C \tag{7.32}$$

etc.

These equations, obtained in a somewhat different way by B. Kudryavtsev (1940), were checked by him on a number of substances. Although Eq. (7.32) is more accurate than Eq. (7.31), it is better to use the latter, because the gain in accuracy is not so great and is overbalanced by the excessive expenditure of time.

It is easy to find the constants of Eq. (7.31) from the graph $\Delta S_{vap} = \varphi(\ln T)$ (Fig. 63). It is more reliable to plot the graph on the basis of several values of ΔH_{vap}. If two points are used, one of which corresponds to a temperature close to T_{er}, then the found equation may not be accurate enough, since Eqs. (7.31) and (7.32)

give good results (an error of $\leqslant 2\%$) only to temperatures that differ from T_{cr} by 20-30 kelvins. In direct proximity to T_{cr}, these equations give unsatisfactory results — here the assumption that ΔC_{eq} depends linearly on T and moreover that ΔC_{eq} is constant loses its meaning.

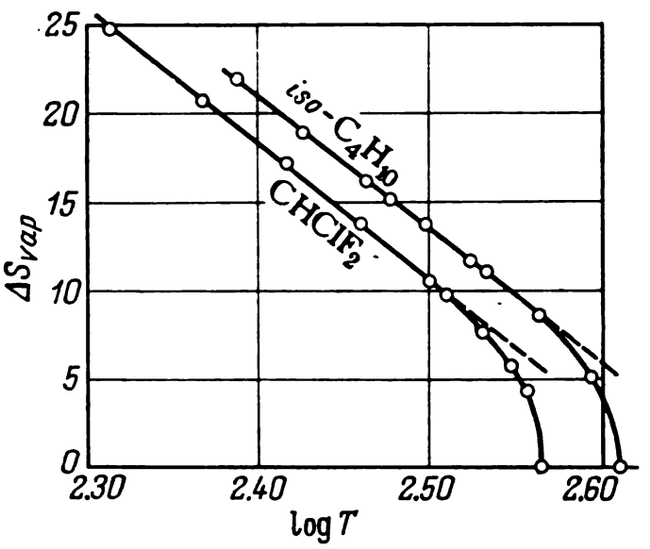

Fig. 63. Dependence of $\Delta S_{vap}=\Delta H_{vap}/T_b$ on logarithm of absolute temperature. Checking of Eq. (7.31). (See Example 13)

The author proposed (1945) an approximate method of calculations whose idea was prompted by the similarity of the curves $\Delta H_{vap} = \varphi(T)$: if straightening out of the curves according to a standard substance (see, for example, the plotting of the lines in Fig. 55) can give acceptable results only for substances with close critical temperatures, then straightening out of these curves after transferring them along the axis of abscissas to a single point ($t_{cr} - t = 0$, $\Delta H_{vap} = 0$) gives satisfactory results up to t_{cr} (Fig. 64).

This method permits us to assess the given relationship if we know T_{cr} and ΔH_{vap} for a given substance at any single temperature, and also know T_{cr} and $\Delta H_{vap} = \varphi(T)$ for the standard substance.

For approximate calculations and in the absence of experimental data, we can take the heat of vaporization at the normal boiling point as the single value for the substance being studied. This quantity can be found according to **Trouton's rule**

$$(\Delta S_{vap})_{n.b.p.} = \frac{(\Delta H_{vap})_{n.b.p.}}{T_{n.b.p.}} \approx 21.3 \qquad (7.33)$$

Calculations of $(\Delta S_{vap})_{n.b.p.}$ for 320 substances have shown that for more than 250 the deviation of the value of $(\Delta S_{vap})_{n.b.p.}$ from 21.3 e.u. does not exceed $\pm 7\%$ (Fig. 65, the shaded area corresponds to this error). The limit of these fluctuations will probably diminish if (1) we exclude beforehand polar and associated liquids, and also ones containing the NH group, for which the values of $(\Delta S_{vap})_{n.b.p.}$ are high, as well as liquids whose vapour is associated [for them $(\Delta S_{vap})_{n.b.p.} < 21.3$] ; and (2) we take account of the vast number of substances which have not yet been studied; we can estimate this number if we consider the number of isomers of any hydrocarbon.

Equation (7.33) not only permits us to assess the value of the heat of vaporization, but also helps us to detect the association of substances. It is hardly expedient to use any of the numerous formulas $(\Delta S_{vap})_{n.b.p.} = (\Delta H_{vap})_{n.b.p.}/T_{n.b.p.} = \varphi(T_{n.b.p.})$ proposed for

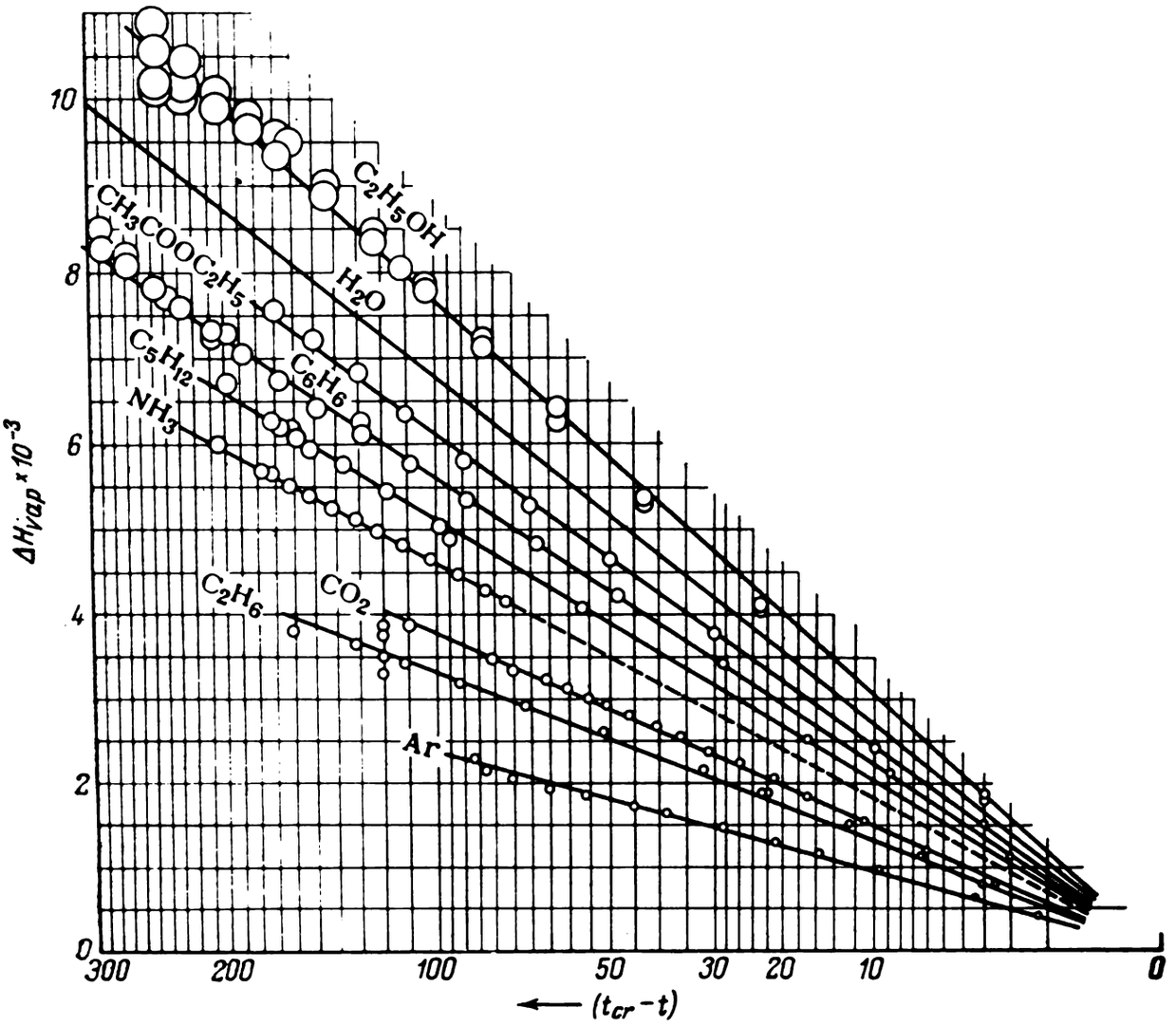

Fig. 64. Temperature dependence of heat of vaporization for selected liquids. Checking of Eq. (7.34). The diameter of the circles used to note the experimental data corresponds to an error of ±2% of the value of ΔH_{vap}. (See Example 14)

making Eq. (7.33) more precise; this is clearly shown by Fig. 65. For related substances, however, one of the methods of comparative calculation [B45] can be used in the form of the relationship

$$[(\Delta S_{vap})_{n.b.p.}]_{II} \approx A\,[(\Delta S_{vap})_{n.b.p.}]_{I} + B \qquad (7.34)$$

Trouton's rule can be considered as a particular case of Eq. (7.34) in which $A = 1$ and $B = 0$. An example of Eq. (7.34) is

$$[(\Delta S_{vap})_{n.b.p.}]_{iso} \approx 1.294\ [(\Delta S_{vap})_{n.b.p.}]_{n} - 6.235$$

where the subscripts *iso* and *n* stand for *iso*-C_nH_{2n+2} and *n*-C_nH_{2n+2}, respectively.

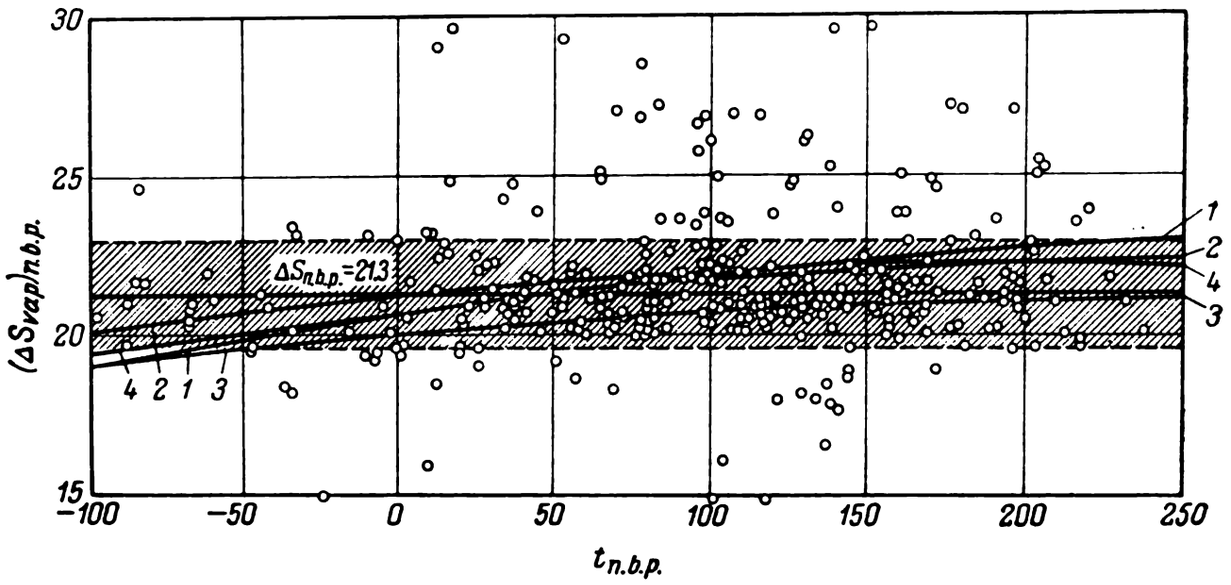

Fig. 65. Change in entropy of various substances at the normal boiling point: *1* – $(\Delta S_{vap})_{n.b.p.} = 8.5 \log T_{n.b.p.}$; *2* – $(\Delta S_{vap})_{n.b.p.} = 9.5 \log T_{n.b.p.} - 0.007 T_{n.b.p.}$; *3* – $(\Delta S_{vap})_{n.b.p.} = 4.571 \log T_{n.b.p.} + 8.75$; *4* – $(\Delta S_{vap})_{n.b.p.} = 10.1 \log T_{n.b.p.} - 1.5 - 0.009 T_{n.b.p.} + 0.000\,000\,26 T^2_{n.b.p.}$
Checking of Eq. (7.33)

The author's method (p. 236) corresponds to the assumption that the ratios of the heats of vaporization of any two substances 1 and 2 are approximately constant at temperatures equidistant from the corresponding critical temperatures:

$$(\Delta H_{vap})_2 \approx C(\Delta H_{vap})_1 \quad \text{at} \quad (t_{cr} - t)_2 = (t_{cr} - t)_1 \qquad (7.35)$$

The values of the constant C for selected substances are given in Table 9.

Water is an appropriate standard substance, since, first, the relationship $\Delta H_{vap} = \varphi(T)$ is known for it with sufficient accuracy and can be found in various reference books; second, for water equilibrium between the liquid and its vapour is observed within quite a broad temperature interval, which makes it possible to graduate the temperature axis according to a single substance up to very great values of $(t_{cr} - t)$. The values of the heat of vaporization of water needed for the calculations are given in Table 10. Intermediate values can be approximately determined by linear interpolation.

The mean error of calculations for 50 substances up to t_{cr} was found to equal about 2% (for purposes of illustration the diameter of the circles in Fig. 64 is taken equal to this value). It exceeded 4% only for CH_4, C_2H_4 and C_3H_7OH.

The properties of related compounds always change according to a known law. The constant C in Eq. (7.35) also changes in a definite

Table 9. **Values of Constant C in Eq. (7.35) for Selected Substances ($C_{H_2O} = 1$)**

Substance	C	Substance	C
Ar	0.235	$C_{12}H_{26}$	1.12
Kr	0.355	CH_3OH	1.01
Cl_2	0.272	C_2H_5OH	1.13
N_2	0.273	C_3H_7OH	1.17
O_2	0.281	CH_3COCH_3	0.856
CO	0.273	$C_2H_5OC_2H_5$	0.772
CO_2	0.560	CH_3COOH	0.679
CS_2	0.698	$HCOOCH_3$	0.778
HCl	0.520	$HCOOC_2H_5$	0.827
NH_3	0.678	CH_3COOCH_3	0.862
N_2O	0.523	$HCOOC_3H_7$	0.888
PH_3	0.480	$CH_3COOC_2H_5$	0.901
SO_2	0.730	$C_2H_5COOCH_3$	0.900
SO_3	0.950	$CH_3COOC_3H_7$	0.938
$SbCl_3$	1.26	$C_2H_5COOC_2H_5$	0.957
$SnCl_4$	0.898	$CH_3CH(CH_3)CH_2COOCH_3$	0.920
CH_4	0.354	$C_4H_9COOCH_3$	0.945
C_2H_2	0.538	CCl_2FCClF_2	0.800
C_6H_6	0.827	CH_3Cl	0.637
C_6H_{14}, 2,2-dimethylbutane	0.800	C_2H_5Cl	0.725
C_8H_{18}, 2,2-dimethylhexane	0.915	C_6H_5Br	0.939
C_9H_{20}	1.02	C_6H_5Cl	0.917
$C_{10}H_{22}$	1.06	C_6H_5F	0.843
$C_{11}H_{24}$	1.09	C_6H_5I	0.993

Approximate Equations for Selected Homologous Series

Homologous series	C
C_nH_{2n+2}, paraffins (alkanes)	$0.50 + 0.08\ (n - 2)$; $n = 2$ to 8
C_nH_{2n+2}, 2-methylalkanes	$0.64 + 0.08\ (n - 4)$; $n = 4$ to 8
C_nH_{2n}, α-olefins	$0.515 + 0.075\ (n - 2)$; $n = 4$ to 8
C_nH_{2n}, naphthenes	$0.64 + 0.06\ (n - 3)$; $n = 3$ to 8
Chlorofluoro-substituted compounds of methane	$0.82 - 0.09n_F - 0.01n_{H'} - 0.05n_{H''} - 0.12n_{H'''}^{*}$

* The value of 0.82 corresponds to C for CCl_4; n_F is the number of fluorine atoms in the compound; $n_{H'}$, $n_{H''}$ and $n_{H'''}$ are respectively the first, second and third atoms of hydrogen introduced into the CCl_4 molecule.

Table 10. **Temperature Dependence of Molar Heat of Vaporization of Water (t_{cr} = 374.15 °C)**

$t_{cr} - t$	ΔH_{vap}	$t_{cr} - t$	ΔH_{vap}	$t_{cr} - t$	ΔH_{vap}	$t_{cr} - t$	ΔH_{vap}
0.5	780	9	2580	40	4710	160	8100
1	1060	10	2680	45	4940	170	8270
1.5	1250	12	2890	50	5155	180	8430
2	1410	14	3080	60	5545	190	8590
2.5	1540	16	3255	70	5910	200	8740
3	1660	18	3415	80	6230	220	9030
3.5	1465	20	3560	90	6525	240	9290
4	1680	22	3700	100	6800	260	9530
4.5	1950	24	3830	110	7055	280	9760
5	2040	26	3960	120	7290	300	9975
6	2190	28	4080	130	7515	320	10 180
7	2330	30	4195	140	7710	340	10 385
8	2460	35	4470	150	7915	360	10 580

order for similar substances (Fig. 66 and Table 9); this allows us to find the temperature dependence of ΔH_{vap} for a member of the given homologous series in the absence of experimental data for it. When extrapolation is used, the results of the calculations should be considered approximate, while for interpolation they are just about as reliable as the data on which the calculations are based.

Apart from Eq. (7.35), an example of the fourth method of approximate calculations is the approximate relationship [B45]

$$(\Delta H_{vap})_2 = A(\Delta H_{vap})_1 + B \qquad (7.36)$$

in which the heats of vaporization of two liquids are compared at an equal vapour pressure ($p_2 = p_1$); for substances with close critical pressures $B \approx 0$ (Fig. 67, p_{cr} for $C_6H_6 \approx p_{cr}$ for $CHClF_2 \approx 48.5$).

It is very convenient to use the values of $(\Delta H^\circ_{298})_{vap}$ for various calculations, since $(\Delta H^\circ_{298})_{vap} = (\Delta H^\circ_{298})^g - (\Delta H^\circ_{298})^{lq}$. The values of ΔH_{vap} differ from ΔH°_{vap}, because the second quantity relates not to equilibrium conditions, but to conditions of transition from the standard state of the liquid (or crystal in the case of sublimation) to the standard state of an ideal gas (and not the saturated vapour). For low pressures (assuming that the laws for ideal gases can be applied to a saturated vapour), we can consider that $\Delta H_{vap} \approx \approx \Delta H^\circ_{vap}$. Thus, for water vapour $(\Delta H_{vap})_{298} = 10\,767$ cal/mol, while $(\Delta H^\circ_{vap})_{298} = 10\,719$ cal/mol. For high pressures and especially for polar liquids, however, this assumption leads only to approximate results.

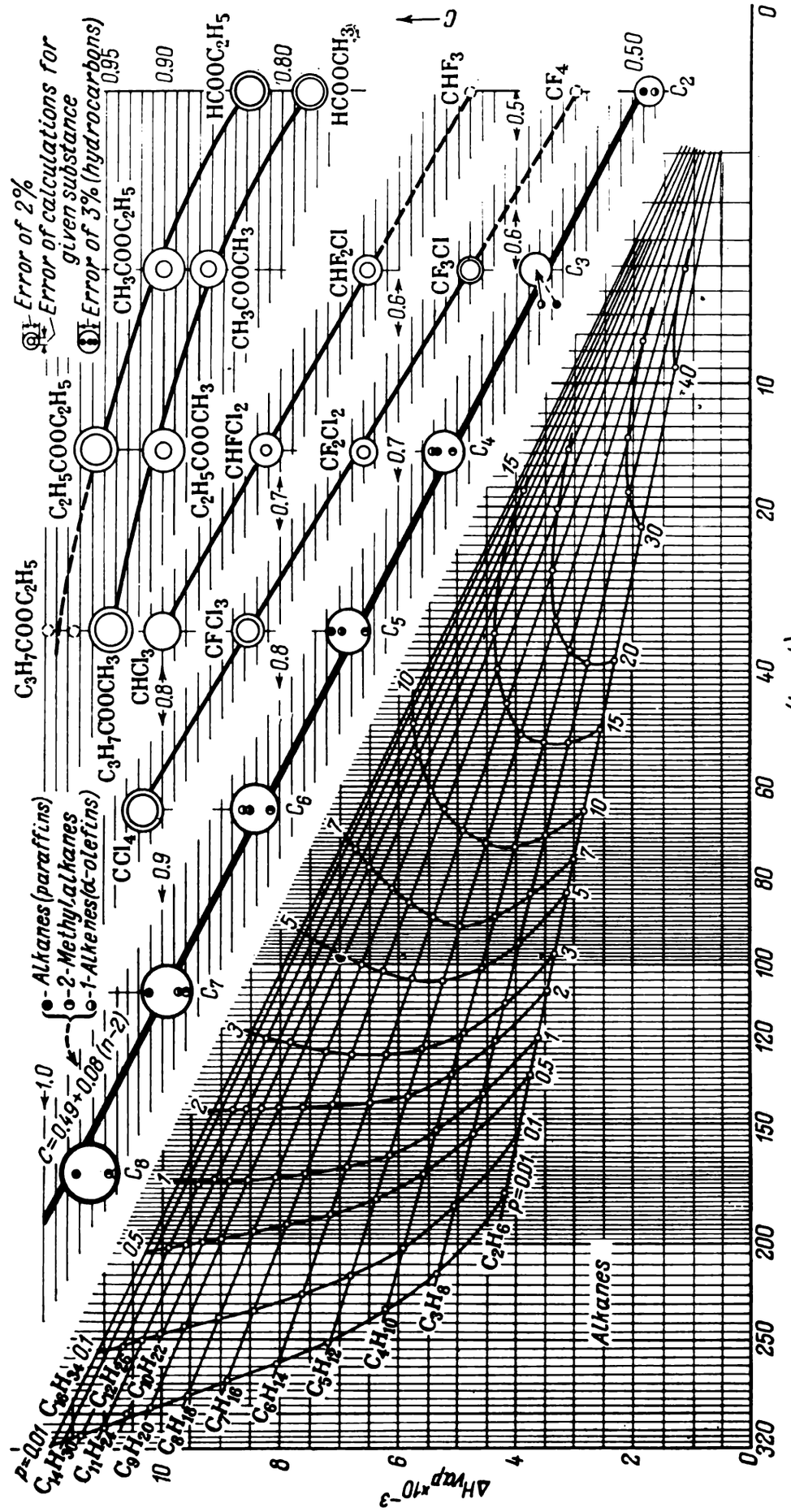

Fig. 66. Temperature dependence of heat of vaporization for selected homologous series.
Checking of the regular change in the constant C of Eq. (7.35) in homologous series

The differences between ΔS_{vap} and ΔS°_{vap} may be even greater, since

$$\Delta S^{\circ}_{vap} = \frac{\Delta H^{\circ}_{vap}}{T_b} + R \ln p$$

or in accordance with the fact that $\Delta H_{vap} \approx \Delta H^{\circ}_{vap}$

$$\Delta S^{\circ}_{vap} = \Delta S_{vap} + R \ln p \qquad (7.37)$$

It follows from the latter relationship that the more T differs from $T_{n.b.p.}$, the greater is the difference between ΔS°_{vap} and ΔS_{vap}. Therefore, if, for example, $(\Delta S_{vap})_{n.b.p.}$ changes only slightly in a homologous series, then $(\Delta S^{\circ}_{vap})_{n.b.p.}$ changes quite considerably (Fig. 68).

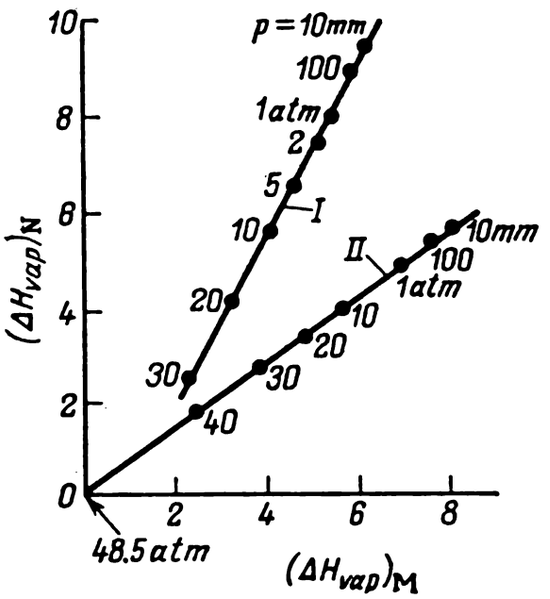

Fig. 67. Relationship between heats of vaporization for equal values of the saturated vapour pressure:
I – butene-1(M) and $C_2H_5COOC_2H_5$(N);
II – C_6H_6(M) and $CHClF_2$(N)

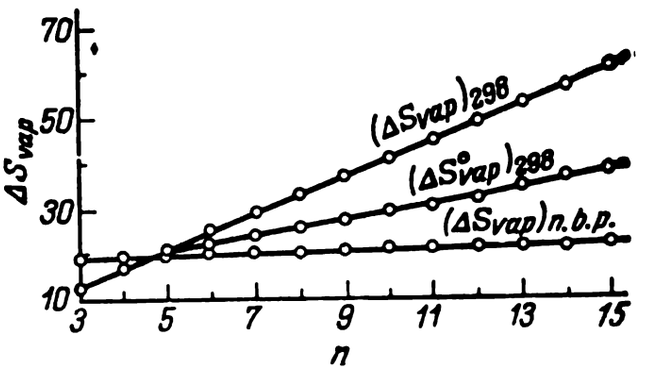

Fig. 68. Dependence of entropy of vaporization on the number of carbon atoms in a molecule of an *n*-alkane C_nH_{2n+2}

Example 13. On the basis of experimental data on the temperature dependence of ΔH_{vap} for isobutane, find the equation $\Delta H_{vap} = \varphi(T)$, taking a form corresponding to Eq. (7.31):

T	244.3	266.5	290.4	299.8	315.0	333.3	341.1	356.6	392.0
ΔH_{vap}	5344	5022	4676	4543	4311	3881	3781	3142	2021

Solution. Using the above data to calculate log T and $\Delta H_{vap}/T$, we find :

log T	2.3879	2.4257	2.4630	2.4768	2.4983	2.5228	2.5329	2.5522	2.5933
$\Delta H_{vap}/T$ ..	21.88	18.84	16.10	15.15	13.68	11.64	11.08	8.81	5.16

We plot a graph in the coordinates $\Delta S_{vap} = \Delta H_{vap}/T = \varphi(\log T)$ (see Fig. 63), from which we determine the constants A and B of Eq. (7.31). We finally get $\Delta H_{vap}/T = 200.9 - 75 \log T$. If we exclude the last experimental value, then summation of the deviations of the experimental points from the straight line gives a mean error of 0.9%.

Example 14. Find ΔH_{vap} of benzene within the interval of 20 to 280 °C (for steps of 20 kelvins) (1) with the aid of Fig. 64, and (2) by Eq. (7.35) if ΔH_{vap} at $t = 80$ °C is 7300 cal/mol. Compare the results of the calculations with reference data (for instance [D4], **8** : 831).

Solution. 1. On the basis of the data given in Table 10, we plot a straightened graph of $(\Delta H_{vap})_w = \varphi(t_{cr} - t)$ (see Fig. 64). Next at a distance of $(t_{cr} - t)_{benz} = 288.5 - 80 = 208.5$ from the origin of coordinates we lay off upward $(\Delta H_{vap})_{benz} = 7300$ and connect the point obtained with the origin of coordinates. (The subscripts "w" and "benz" stand for water and benzene, respectively.) We read off the values of $(\Delta H_{vap})_{benz}$ at different temperatures from this straight line.

2. From Table 10 we find $(\Delta H_{vap})_w$ at a temperature removed from the critical one (Appendix 9) by $(t_{cr} - t)_{benz} = 208.5$ [i.e. at $(374.2 - 208.5)_w = 165.7$ °C]. We get $(\Delta H_{vap})_w$ at this temperature equal to 8860 cal/mol. Hence, the constant C in Eq. (7.35) equals 7300/8860 = 0.824. We calculate $(\Delta H_{vap})_{benz}$ for $t = 160$ °C, i.e. for $(t_{cr} - t)_{benz} = (t_{cr} - t)_w = 288.5 - 160 = 128.5$. From Table 10 we find $(\Delta H_{vap})_w \approx 7480$, and by Eq. (7.35) we get $(\Delta H_{vap})_{benz} = 0.824 \times 7480 = 6164$ cal/mol.

In a similar way, we determine $(\Delta H_{vap})_{benz}$ for $t = 20$, 40, 60, 80, etc.

The mean deviation of the calculated data from the values given in a reference book [D4] is 1.4%.

Example 15. Determine ΔH_{vap} for octane at 240 °C if $t_{n.b.p.} = 125.6$ °C. Use the data given in Appendix 9 and Tables 9 and 10 for the calculations.

Solution. We find $t_{cr} - t = 56.7$. From Table 10 for this value we determine $(\Delta H_{vap})_w \approx 5400$ cal/mol. According to the equation

for alkanes (see Table 9), we have $C = 0.50 + 0.08 \times 6 = 0.98$. Hence for octane ($C_8H_{18}$), we get $\Delta H_{vap} = 0.98 \times 5400 = 5292$, which differs from the experimentally found value (5250) by 0.8%.

Heat and Entropy of Melting. The change in the molar entropy in melting is not so constant as in vaporization. Therefore, there are no relationships similar to Eq. (7.33) which in the first approximation would hold for all substances. Attempts to calculate the heats of melting according to the values of π and τ do not give positive results, since in contrast to vaporization, the principle of corresponding states is not correct for melting. On the basis of experimental data, however, we can often assume that

$$\Delta S_{el} \approx 2\text{-}3, \quad \Delta S_{inorg.comp} \approx 5\text{-}7, \quad \Delta S_{org.comp} \approx 13 \pm 3 \qquad (7.38)$$

These expressions can be used for calculations only as a rough approximation in the absence of experimental data.

7.5. INFLUENCE OF TOTAL PRESSURE ON SATURATED VAPOUR PRESSURE

Consider a liquid (solid) in equilibrium with its vapour and subjected to isothermal compression.

In Eq. (5.47) $n = 3$, since apart from p and T we have to take the external pressure p_{ext} into consideration. Therefore $f = 2$, i.e. $p = \varphi(T, p_{ext})$ and $p_T = \varphi(p_{ext})$. Compression actually occurs not with the aid of a semipermeable piston (letting through the vapour and retaining the condensed phase), but with the aid of an inert gas, i.e. a gas insoluble in the liquid. The result does not change: if we consider the system as a two-component one and the inert gas to be a part of it, then in Eq. (5.47) we have $n = 2$ and as previously $f = 2$.

It thus follows from the phase rule that p_{ext} *affects* p. To find out how the vapour pressure will change, we have to revert to the principle of displacement of equilibrium. The introduction of a gas insoluble in the liquid into the system violates equilibrium, and the molecules of the liquid pass over into the vapour phase. Here the concentration of vapour, reduced as a result of the introduction of molecules of the inert gas, grows. The increase in the concentration of the vapour of the liquid in a compressed gas may only be due to molecules of the liquid passing over into the vapour phase. The growth of the pressure on a liquid is thus attended by an increase in its vapour pressure.

Let us now solve the problem *quantitatively*.

When the pressure grows by dp_{ext}, the newly established equilibrium will be characterized by the equality $dG^{lq} = dG^{g}$, or by Eq. (5.25)

$$V^{lq}\, dp_{ext} = V^{g}\, dp$$

i.e.

$$\left(\frac{\partial p}{\partial p_{ext}}\right)_T = \frac{V^{lq}}{V^{g}} \tag{7.39}$$

At temperatures sufficiently removed from the critical ones, we have $V^{g} \gg V^{lq}$ [for example for water $(V^{lq}/V^{g})_{p=1,\, t=100} = 0.000\,624$], and consequently p grows negligibly with p_{ext}. In other words, for a small external pressure, the saturated vapour pressure has practically the same value as in the absence of a gas over the liquid and can be calculated by the Clapeyron-Clausius equation. (The fact that p does not depend on p_{ext} at low pressures is a corollary of Dalton's law. The only difference from vaporization in a vacuum consists in that in the presence of an inert gas, equilibrium between a liquid and its vapour sets in at a considerably slower rate owing to the retarded diffusion. This is due not only to the presence of molecules of the inert gas, but also to an increase in the internal friction of gases with a growth in the external pressure.)

If we assume as a first approximation that the Mendeleev-Clapeyron equation holds for a vapour, then Eq. (7.39) becomes

$$\left(\frac{\partial \ln p}{\partial p_{ext}}\right)_T = \frac{V^{lq}}{RT} \tag{7.40}$$

Integrating Eq. (7.40) and assuming that $V^{lq} = \text{const}$, we get

$$\ln \frac{p_2}{p_1} = \frac{V^{lq}}{RT}\left[(p_{ext})_2 - (p_{ext})_1\right] \quad \text{or} \quad \ln \frac{p'}{p} = \frac{V^{lq}}{RT}\left(p'_{ext} - 1\right) \tag{7.41}$$

where p is the saturated vapour pressure in the absence of an inert gas.

This equation can be obtained directly from Eq. (6.38), and Eq. (7.40) directly from Eq. (6.32).

When assessing the accuracy of Eq. (7.41), one should bear in mind that the deviation from it becomes significant even at moderate pressures. This is due less to the inaccuracy of the Mendeleev-Clapeyron equation than to superposition on the effect being considered of another effect. The latter also changes quantitatively with the pressure and consists in solution of a liquid in a compressed gas (see Sec. 9.3), when the major part is played by the action of inter-

molecular forces and by the specific nature of the inert gas as a solvent. Hence, despite Eq. (7.41), the increase in the vapour pressure depends on the nature of the inert gas. The considerable influence of both effects can be seen in Fig. 69, which shows the results of a number of experiments; the concentration of water

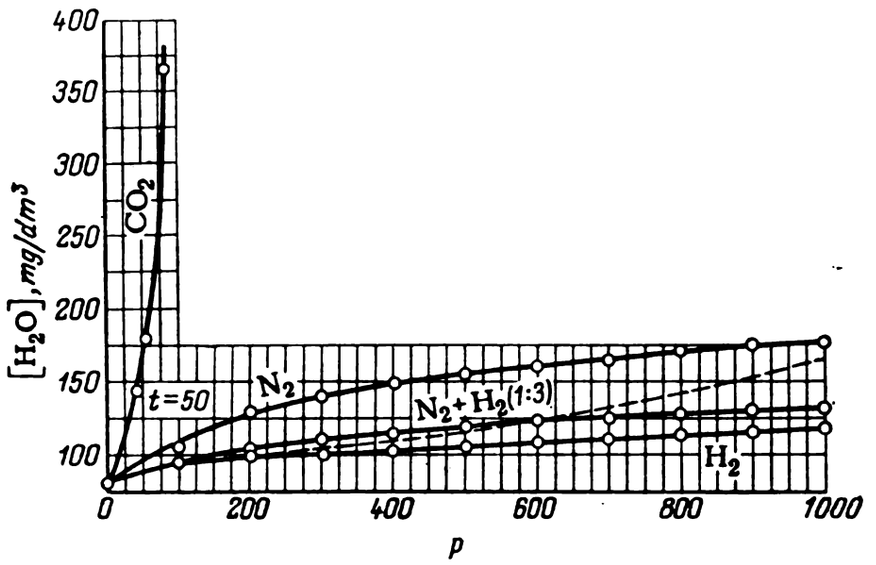

Fig. 69. Dependence of concentration of water vapour in compressed gases on the external pressure.
Checking of Eq. (7.38)

vapour in the compressed gas, which is proportional to the vapour pressure, is laid off along the axis of ordinates. The dashed line is a theoretical one corresponding to Eq. (7.41).

It can be assumed that one of the causes of catalyst poisoning in the conducting of synthesis (for example ammonia synthesis) under pressure is oil getting into the gas mixture. At a very high pressure, it may not be completely separated from the gas in the oil separator and remairs in the gas not in the form of drops of liquid, but as a vapour.* Experiments show that the concentration of oil in a greatly compressed gas is quite significant. Thus, the solubility of compressor oil in nitrogen at 150 °C grows 45 times when the pressure is increased from 100 to 900 atm.

A similar effect is also observed for solids under the action of very high pressures. The solubility of solids in greatly compressed gases was quite significant not long ago for the operation of high-pressure boilers. One of the possible reasons for the reduction in the output of steam power plants was the carry-over (not mechanical!) of salts from the boiler with the steam ($p > 100$ atm, $t > 400$ °C), and especially of silicon dioxide. These salts, being deposited (upon

* Recently turbocompressors, which in contrast to piston compressors operate without lubrication, have been introduced.

expansion of the steam) on the turbine blades, constrict the passages of the ducts, distort their profile, and reduce the efficiency and power of the turbine. *

Example 16. Find the concentration of water vapour in a compressed gas at $t = 50\,^{\circ}C$ and $p = 100$ atm if 1 dm^3 of the compressed gas at the saturated vapour pressure contains 82.94 mg of vapour. Compare the value obtained with the one found experimentally for H_2 and N_2 (see Fig. 69).

Solution. It follows from Eq. (7.41) that

$$\ln \frac{p'}{p} = \frac{18(100 - 1)}{82.06 \times 323.2}$$

whence $p'/p = 1.07$. Since the concentration of the vapour in the compressed gas is proportional to the increase in its pressure, the required quantity equals $82.94 \times 1.07 = 88.7$ mg/dm^3.

Comparison with the data given in Fig. 69 (about 90 atm for H_2 and 106 for N_2) shows that deviation from Eq. (7.41) is observed and that water vapour dissolves better in compressed nitrogen than in compressed hydrogen.

7.6. INFLUENCE OF SURFACE CURVATURE ON SATURATED VAPOUR PRESSURE

The pressure of a vapour also depends on the curvature of a surface.

A liquid in the form of drops has a surplus surface energy in comparison with a large mass of liquid having a flat surface. This surplus energy is the greater, the smaller is the radius of curvature. It manifests itself in a growth in vapour pressure as the size of the liquid drops diminishes; this explains the coalescence of small droplets and the condensation of vapour on particles of dust.

Consider the transition of a liquid from drops to a large mass. The volume of a drop equals $nV = \frac{4}{3}\pi r^3$. A change in the mass of a drop by dn moles results in a change in its radius by $dr = Vdn/4\pi r^2$, and of its surface area $A = 4\pi r^2$ by $dA = 8\pi r\, dr$.

If we denote by G and G' the molar Gibbs energy in a drop and in a large mass of a liquid, respectively ($G > G'$), the process of transfer of dn moles of the liquid (disregarding the change in the surface area of the large mass of the liquid) will involve a change in the Gibbs energy $(G - G')dn = \sigma dA$ (where σ is the surface tension).

* This difficulty vanished when water having a very high purity began to be used.

Using in this equation the values of dn and dA and reducing the change in the Gibbs energy to one mole, we get the **Thomson equation** (1871) *

$$\Delta G = RT \ln \frac{p_{\text{droplet}}}{p} = \frac{2\sigma V}{r} \qquad (7.42)$$

(If σ is expressed in erg/cm^2 and R in cal/mol·K, then the factor 4.184×10^7 should be introduced into the denominator.)

For a concave surface, the calculations are performed by Eq. (7.42) with a minus sign placed before its right-hand side (the pressure of a vapour over a concave surface is less than over a flat one). The smaller vapour pressure leads to condensation in capillaries at lower pressures than on an open surface (the phenomenon of **capillary condensation**). This also explains the hygroscopicity of substances.

If the tendency of a substance to pass into a solution is treated similar to evaporation, equations similar to Eq. (7.42) can be used to explain the consolidation of fine precipitates when they are left standing, the higher melting point of large precipitates in comparison with that of smaller ones, etc. (see also Sec. 9.4).

Equation (7.42) is approximate, since it assumes the ideal nature of the supersaturated vapour and the lack of dependence of the surface tension on the radius of the droplets. It was determined more precisely by S. Gorbachev (1935), who considered a supersaturated vapour as a gas for which Eq. (6.19) holds.

In connection with studying the phenomena associated with the formation of a new phase, Gorbachev (1941) derived approximate equations for calculating the influence of the radius of liquid droplets on the freezing point and of the dimensions of crystals on the melting point. In making these relationships more accurate, he also worked out methods of calculating the influence of the pressure and temperature on ΔH, ΔV and $\partial p/\partial T$ attending phase transitions. These equations make it possible to calculate equilibria with the aid of the directly measured physical properties of a substance in equilibrium phases $[(\partial V/\partial p)_T$, $(\partial V/\partial T)_p$ and $(\partial p/\partial T)_V]$, and also the reverse problem — to find its mechanical and thermomechanical properties.

Example 17. How much less is the pressure of water vapour over a flat surface than over a spherical one if the radius of curvature of the latter is 10^{-6} cm, $T = 300$ K and $\sigma_{H_2O} = 75$ erg/cm^2?

* The relationship between the vapour pressure over a horizontal surface and the vapour pressure under the action of a force, which Eq. (7.42) follows from as a particular case, was proposed by N. Shiller (1894).

Solution. It follows from Eq. (7.42) that

$$\ln \frac{p_{\text{droplet}}}{p} = \frac{2\sigma V}{4.184 \times 10^7 RTr} = \frac{2 \times 75 \times 18}{4.184 \times 10^7 \times 1.987 \times 300 \times 10^{-6}}$$

whence $p_{\text{droplet}}/p = 1.115$, i.e. for condensation of droplets of water of the given size a pressure 11.5% greater than that needed for condensation on a flat surface would be required.

For very tiny particles, such calculations may give incorrect results, because the number of molecules in a droplet becomes so insignificant that the surface tension σ may change; in addition, thermodynamic methods generally cannot be applied to such particles.

7.7. SECOND-ORDER PHASE TRANSITIONS

Equation (7.1) describes first-order phase transitions characterized by a continuous change in the Gibbs energy and a stepwise change in its first derivatives, i.e. volume and entropy. There are **second-order phase transitions,** which differ from the above in the continuous change in G, V [i.e. $(\partial G/\partial p)_T$] and S [i.e. $(\partial G/\partial T)_p$], but in a stepwise change in $(\partial^2 G/\partial p^2)_T = (\partial V/\partial p)_T = -\gamma V$, $(\partial^2 G/\partial T^2)_p = -C_p/T$ and $\partial^2 G/\partial p\, \partial T = -(\partial V/\partial T)_p = \alpha V$, where γ is the isochoric pressure coefficient and α is the isobaric expansion coefficient. In second-order transitions, the first derivatives of a thermodynamic parameter are continuous, but the second derivatives with respect to the corresponding parameters change in steps. Such transitions are not attended by a heat effect and are characterized by a change in the heat capacity, expansion and pressure coefficients, i.e. the coexisting phases differ not in volume and their store of energy, but in the values of their derivatives. In contrast to a first-order transition, a metastable state near the transition points is impossible for a second-order transition. The latter occur in crystals when they transform from one kind of symmetry to another, when ferromagnetic substances (for example iron) transform into paramagnetic ones, when a metal (for example lead) transforms into a superconducting state, and when helium I transforms into helium II. A first-order transition is also characterized by features typical of a second-order transition at the critical point.

Differentiating $\Delta(\partial G/\partial T)_p = 0$ and $\Delta(\partial G/\partial p)_T = 0$ with respect to T and p, we get

$$\Delta\left(\frac{\partial^2 G}{\partial T^2}\right)_p dT + \Delta\left(\frac{\partial^2 G}{\partial T\, \partial p}\right)_p dp = 0$$

and

$$\Delta\left(\frac{\partial^2 G}{\partial p\,\partial T}\right)_T dT + \Delta\left(\frac{\partial^2 G}{\partial p^2}\right)_T dp = 0$$

or in accordance with the values of the second derivatives

$$\left.\begin{aligned} -\left(\frac{\Delta C_p}{T}\right)_p dT + \Delta\left(\frac{\partial V}{\partial T}\right)_p dp = 0 \\ \Delta\left(\frac{\partial V}{\partial T}\right)_T dT + \Delta\left(\frac{\partial V}{\partial p}\right)_T dp = 0 \end{aligned}\right\} \tag{7.43}$$

whence after excluding dp and dT we find

$$\Delta C_p \Delta\left(\frac{\partial V}{\partial p}\right)_T dp + T\left[\Delta\left(\frac{\partial V}{\partial T}\right)_p\right]^2 = 0 \tag{7.44}$$

Equations (7.43) and (7.44) were derived by P. Ehrenfest (1933), who established the existence of second-order phase transitions. Equation (7.44) is an analogue of Eq. (7.1).

Chapter 8

SOLUTIONS

8.1. FUNDAMENTAL CONCEPTS AND DEFINITIONS

A **solution** is a thermodynamically stable homogeneous system of a varying composition — a solid, liquid or gas — including at least two components. Each component is formed by identical or different (for example associated) particles forming a common phase and being in unretarded equilibrium with one another. * Examples of solutions are sea water, air and certain alloys.

All the constituents of a solution are thermodynamically equivalent. Their division into a solvent and solutes has no basic significance and is often hypothetic. Usually the term solvent is used to denote the component predominating in quantity, frequently the one whose addition does not result in heterogenization of the solution. If one of the components in given conditions is in the liquid state of aggregation, while the others are solid and gaseous substances, then the liquid is considered to be the solvent even if the other substances are present in a greater amount.

We shall chiefly treat two-component systems in the following, because, first, they are the simplest systems, and, second, many laws obtained for them can be applied to solutions consisting of a greater number of components. We shall use the subscript 1 to characterize the solvent, and the subscript 2 (3, 4, etc.) to characterize the solute (solutes).

The following ways to express the quantitative composition of a solution are commonly used.

Mole Fractions. In accordance with Eq. (1.9), which expresses the concentration in mole fractions, for a system of k components

$$\left.\begin{aligned} x_1 + x_2 + x_3 + \ldots + x_k &= 1 \\ dx_k = -dx_1 - dx_2 - dx_3 - \ldots - dx_{k-1} & \end{aligned}\right\} \tag{8.1}$$

* In practice we often have to do with solid solutions that are in retarded equilibrium (see, for example p.19).

In certain cases, for example for alloys, the mole fractions become atomic fractions.

Methods of expressing the concentration based on a constant amount of the solution also include the **mass fraction** (the mass of a component in a unit of mass of the solution), the **volume fraction** (the volume of a component in a unit of volume of the solution), and the **molar-volume concentration** (the number of moles of a component in a unit of volume of the solution). When the unit of volume of the solution is a litre (dm^3), the molar-volume concentration is called the **molarity.** The molarity corresponds to expressing the concentration with a constant volume of the solution (the same is true for the normality and titre).*

Concentration is also expressed by relating the amount of a component of the solution to a definite amount of the solvent. Thus the **mole-mass ratio** shows the number of moles of a component per known mass of another component (usually the solvent). This way of expressing the composition is especially often used for aqueous solutions. The unit of mass used is 1000 grammes (55.51 moles) of water; consequently, the **molality**

$$m = \frac{n_2 \times 1000}{w_{H_2O}} = \frac{n_2 \times 1000}{18 n_{H_2O}} \qquad (8.2)$$

The **mole ratio** — the number of moles of a component per mole of another component (usually the solvent) — and also the mass of a solute per unit of mass of the solvent are less frequently used.

The first method is most common (especially in theoretical research), since many properties of solutions can be expressed in the simplest way in relative numbers of molecules.

The use of the molar-volume concentration gives results depending on temperature. This is not particularly convenient when mixing is attended by a change in volume, but its use is recommended for isochoric-isothermal processes.

The solubility of various substances can be compared only when the composition is measured in the same way. The need to do this is illustrated by data on the solubility of sulphur in two solvents at 25 °C:

	x_2	Weight %	g/dm³
Benzene	0.641	2.07	18.5
Toluene	0.735	2.02	17.8

In conclusion, we shall introduce the following concepts:

* If necessary, it is indicated whether a solution is, for example, normal with respect to a reaction of neutralization, oxidation or another reaction.

1. The volume of one mole of a solution is the amount of the latter in which $n_1 + n_2 + n_3 + \ldots = 1$.

2. The **average molecular mass (weight)** of a solution

$$M_{av} = \Sigma x_i M_i \tag{8.3}$$

Example 1. The solubility of naphthalene ($C_{10}H_8$) in benzene (C_6H_6) at 20 °C is 34.3 weight %. Find its mole fraction.

Solution. According to Eq. (1.9)

$$x_{naph} = \frac{34.3/128}{34.3/128 + 65.7/78} = 0.241$$

It is easy to obtain the same result with the aid of a nomogram (Fig. 70). For this purpose, connect the point $M_2 = M_{naph} = 128$ (the first scale) to the point $M_1 = M_{benz} = 78$ (the third scale), and on the second scale we find $M_2/M_1 = 1.64$. Now connecting this point to the point 34.3% on the fifth scale, we find the answer on the fourth scale — 24 mole %, i.e. $x_2 = 0.24$.

Example 2. At 20 °C, the density of a 10% aqueous solution of methyl alcohol is 0.9815 g/cm³. Express the concentration of the solution in different units.

Solution. 100 cm³ of the solution, with a mass of 98.15 g, contain $0.10 \times 98.15 = 9.82$ g, or $9.82/32 = 0.31$ mol of CH_3OH, and $98.15 - 9.82 = 88.33$ g, or $88.33/18 = 4.90$ mol of H_2O.

1. The mole fractions of the alcohol and water are, respectively,

$$x_{alc} = \frac{0.31}{0.31 + 4.90} = 0.059 \text{ and } x_w = 1 - 0.059 = 0.941$$

2. The molality of the solution by Eq. (8.2) is

$$m = \frac{0.31 \times 1000}{18 \times 4.90} = 3.51$$

3. The molar-volume concentration is $9.82/32 = 0.31$ mol of alcohol per 100 cm³ of solution.

4. The mass (weight) concentration is $9.82/88.33 = 0.111$ g of CH_3OH per gramme of H_2O.

Example 3. The density of a solution of H_2SO_4 containing five moles of acid per cubic decimetre of solution is 1.2894 g/cm³ at 15 °C. Find the mole fraction of the acid, and the molality and average molecular mass of the solution.

Solution. Five moles of H_2SO_4 have a mass of $5 \times 98 = 490$ g. The mass of the H_2O per dm³ of the solution is $1289.4 - 490 = 799.4$ g, which corresponds to $799.4/18 = 44.41$ moles. Hence

$$m = \frac{5 \times 1000}{799.4} = 6.254 \text{ and } x_{acid} = \frac{6.254}{6.254 + 55.51} = 0.101$$

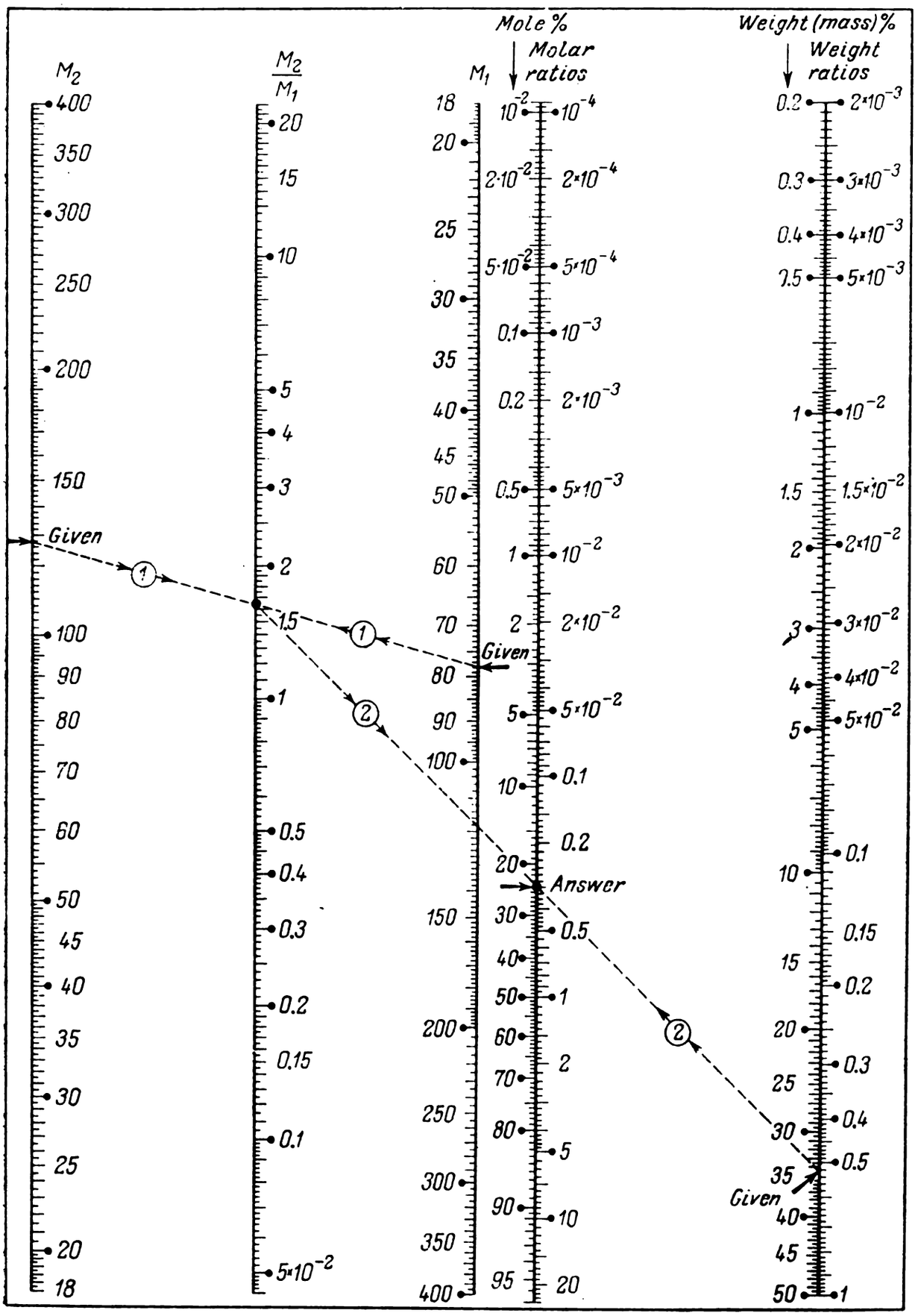

Fig. 70. Nomogram for converting the concentrations of solutions [D114].

The figures in circles indicate the sequence of the operations for solving Example 1

The average molecular mass of the solution by Eq. (8.3) is $M_{av} = 0.101 \times 98 + 0.899 \times 18 = 26.1$.

8.2. PARTIAL MOLAR QUANTITIES

Any *extensive* property of a solution depends on its composition. When a substance is added to a solution, the composition of the latter continuously changes; therefore the *change* in an extensive property of a solution also depends on the composition, i.e. on the amount of substance added. To be able to use an observed change in an extensive property (for example the volume) of a solution to assess the value of this property of a component in a solution having a *given* composition, it is necessary to add such an amount of the substance to the solution which will hardly change its composition. This can be done in two ways (1) by adding one mole of the component to a very large amount of the solution of the given composition; and (2) by adding an infinitely small amount of the component to a finite amount of the solution having the given composition and converting the change in the property obtained to one mole of the substance being added. The change in a property found in this way (assuming that p and T are constant) is called a **partial molar quantity** $\bar{Y}_i$ (G. Lewis, 1907). Consequently,

$$\bar{Y}_i = \left(\frac{\partial Y_{tot}}{\partial n_i}\right)_{p,T,n_j} \tag{8.4}$$

where Y_{tot} = an extensive property of a solution (V, S, U, H, A, G, C_p, C_V)

$\bar{Y}_i$ = corresponding partial molar property of a given component, i.e. $\bar{V}_i$, $\bar{S}_i$, etc. (the subscripts correspond to the conditions of running an experiment, i.e. the constancy of p, T and the composition of the solution).

Thus, when determining the numerical value of a partial molar property of a component of a solution, its composition must always be indicated.

Equations expressing the change in properties with a change in composition are widely used in the thermodynamics of solutions. Therefore, partial molar quantities play the same part in the thermodynamics of solutions as molar quantities in the thermodynamics of pure substances.*

* Back in 1885 D. Mendeleev noted the importance of using derivatives of the properties of a solution with respect to its composition when studying the properties of solutions. M. Vrevsky (1900) used partial molar quantities in the form of differential heats (see Sec. 8.3.2. and p. 328).

If y and z stand for two properties of a pure substance related by the equation

$$y = \frac{\partial Y_{\text{tot}}}{\partial z}$$

then in accordance with Eq. (8.4) we get

$$\overline{y}_i = \frac{\partial y}{\partial n_i} = \frac{\partial}{\partial n_i}\frac{\partial Y_{\text{tot}}}{\partial z} = \frac{\partial}{\partial z}\frac{\partial Y_{\text{tot}}}{\partial n_i} = \frac{\partial \overline{Y}_i}{\partial z}$$

Hence the same equations hold for a component of a solution as for the pure substance, except that the corresponding partial molar properties are used in them instead of the molar properties.

Thus, Eqs. (5.24), (5.25), (6.32) and (6.39) respectively acquire the form

$$\left(\frac{\partial \overline{G}_i}{\partial T}\right)_{p,\,x} = -\overline{S}_i \tag{8.5}$$

$$\left(\frac{\partial \overline{G}_i}{\partial p}\right)_{T,\,x} = \overline{V}_i \tag{8.6}$$

$$\left(\frac{\partial \ln f_i}{\partial p}\right)_{T,\,x} = \frac{\overline{V}_i}{RT} \tag{8.7}$$

$$\left(\frac{\partial \ln f_i}{\partial T}\right)_{p,\,x} = \frac{\overline{H}_i^{\circ} - \overline{H}_i}{RT^2} \tag{8.8}$$

where $\overline{H}_i^{\circ}$ is the partial molar enthalpy of a component in its standard state in the form of an idealized gas (the subscript x indicates that the composition is constant).

If we used Eq. (6.32) to calculate the fugacity of a pure component, we should use Eq. (8.7) to calculate the fugacity of a gas solution (mixture). Expressing the partial molar volume by the equation $\overline{V}_i = V_i - \alpha_i$, i.e. proceeding similar to the derivation of the equation for calculating the fugacity of a pure gas, and integrating Eq. (8.7) within the limits from p^* to p, we get

$$RT \ln \frac{f_i}{f_i^*} = RT \ln \frac{p}{p^*} - \int_0^p \alpha_i \, dp$$

In view of the fact that $p_i^* = f_i^*$, we obtain the following equation in accordance with Dalton's law (6.14)

$$RT \ln f_i = RT \ln p + RT \ln x_i + \int_0^p (\overline{V}_i - V_i) \, dp \tag{8.9}$$

The temperature dependence of f_i for a gas mixture is expressed by Eq. (8.8), where $\overline{H}_i^\circ = H_i$ (since for a mixture of ideal gases $\overline{H}_i = H_i$).

Apparent molar quantities are widely used for calculations relating to binary systems (their use is best for the solute):

$$\Phi_{Y_2} = \frac{Y_{tot} - n_1 Y_1}{n_2}$$

or for an aqueous solution

$$\Phi_{Y_2} = \frac{Y_{tot} - 55.51 Y_1}{m} \tag{8.10}$$

Now the equation for a binary solution $Y_{tot} = n_1 Y_1 + n_2 \Phi_{Y_2}$ formally coincides with the expression showing the additivity of the property Y.

Attention should be drawn to the following circumstances.

1. Partial molar quantities cannot be identified with chemical potentials. This becomes obvious if we compare Eqs. (5.39) and (8.4). Only the partial molar Gibbs energy is a chemical potential.

2. Partial molar quantities express *changes* in properties, and for this reason they cannot be considered similar to the relevant molar quantities. The former may take on such values that are absurd for the latter (thus, partial molar volumes, unlike molar volumes, may be negative and may increase with a growth in pressure).

8.2.1. Basic Equations

From the expression

$$(dY_{tot})_{p,T} = \left(\frac{\partial Y_{tot}}{\partial n_1}\right)_{p,T,n_j} dn_1 + \left(\frac{\partial Y_{tot}}{\partial n_2}\right)_{p,T,n_j} dn_2 + \\ + \ldots + \left(\frac{\partial Y_{tot}}{\partial n_k}\right)_{p,T,n_j} dn_k$$

it follows that

$$(dY_{tot})_{p,T} = \overline{Y}_1 dn_1 + \overline{Y}_2 dn_2 + \ldots + \overline{Y}_k dn_k \tag{8.11}$$

Partial molar quantities depend on the composition of a solution, i.e. are determined by the ratio $n_1 : n_2 : \ldots : n_k$. If at p, T = = const the composition does not change, then the partial molar quantities also remain constant. Therefore, integrating Eq. (8.11) on the condition that $\overline{Y}_1, \overline{Y}_2, \ldots$ = const, which means the addition of all the components in a proportion corresponding to their ratio in the initial solution, we get the equation

$$Y_{tot} = n_1 \overline{Y}_1 + n_2 \overline{Y}_2 + \ldots + n_k \overline{Y}_k \tag{8.12}$$

whose integration constant equals zero, since when n_1, n_2, ..., $n_k = 0$, we also have $Y_{tot} = 0$.

Equation (8.12) can also be obtained by reasoning as follows: if Y_{tot} is an extensive property of a solution containing n_1, n_2, n_3, etc. moles of the components, then by adding n_1 moles of the first component to a very large amount of the solution, the value of the property being studied will increase by $n_1\bar{Y}_1$; the following addition of n_2 moles of the second component will cause the property to grow by $n_2\bar{Y}_2$, etc. The total increment of the property does not depend on the sequence in which the components are added. It equals Y_{tot}, since after all the operations such an amount of the solution of the previous composition should be formed which contains n_1 moles of the first component, n_2 moles of the second, etc.

For one mole of a solution, Eq. (8.11) becomes

$$dY_{p,T} = \bar{Y}_1 dx_1 + \bar{Y}_2 dx_2 + \ldots + \bar{Y}_k dx_k \tag{8.13}$$

For a binary aqueous solution we have

$$Y = 55.51\bar{Y}_1 + m\bar{Y}_2 \tag{8.14}$$

Considering that in Eq. (8.12) both n_1, n_2, etc. and $\bar{Y}_1$, $\bar{Y}_2$, etc. are variables, i.e. assuming that the solution changes its composition, after differentiation we find that

$$(dY_{tot})_{p,T} = n_1 d\bar{Y}_1 + n_2 d\bar{Y}_2 + \ldots + n_k d\bar{Y}_k + \\ + \bar{Y}_1 dn_1 + \bar{Y}_2 dn_2 + \ldots + \bar{Y}_k dn_k \tag{8.15}$$

Solving Eqs. (8.15) and (8.11) simultaneously, we get

$$n_1 d\bar{Y}_1 + n_2 d\bar{Y}_2 + \ldots + n_k d\bar{Y}_k = 0 \tag{8.16}$$

Equations (8.12) and (8.16) are called **Gibbs** (1876)-**Duhem** (1886) **equations.**

For one mole of a solution, Eq. (8.16) becomes

$$x_1 d\bar{Y}_1 + x_2 d\bar{Y}_2 + \ldots + x_k d\bar{Y}_k = 0 \tag{8.17}$$

whose integration makes it possible to find how a partial molar quantity for one of the components depends on the concentration if it is known for the other component (components).

Since the number of independent concentrations is one less than the number of components, then using x_2 as the independent variable, we can write down Eq. (8.17) in the form

$$x_1 \frac{\partial \bar{Y}_1}{\partial x_2} dx_2 + x_2 \frac{\partial \bar{Y}_2}{\partial x_2} dx_2 = 0$$

or after cancelling dx_2 and transformations

$$\frac{\partial \bar{Y}_1/\partial x_2}{\partial \bar{Y}_2/\partial x_2} = -\frac{x_2}{x_1} \tag{8.18}$$

It follows from Eq. (8.18) that:

1. The derivatives $\partial \bar{Y}_1/\partial x_2$ and $\partial \bar{Y}_2/\partial x_2$ always have opposite signs.

2. When $x_1 = x_2 = 0.5$, we have $\partial \bar{Y}_1/\partial x_2 = -\partial \bar{Y}_2/\partial x_2$, i.e. the slopes of the curves $\bar{Y}_1 = \varphi(x_2)$ and $\bar{Y}_2 = \varphi(x_2)$ differ only in sign.

3. If one curve has a maximum, the other curve has a minimum for the same composition.

These conclusions are illustrated in Fig. 71.

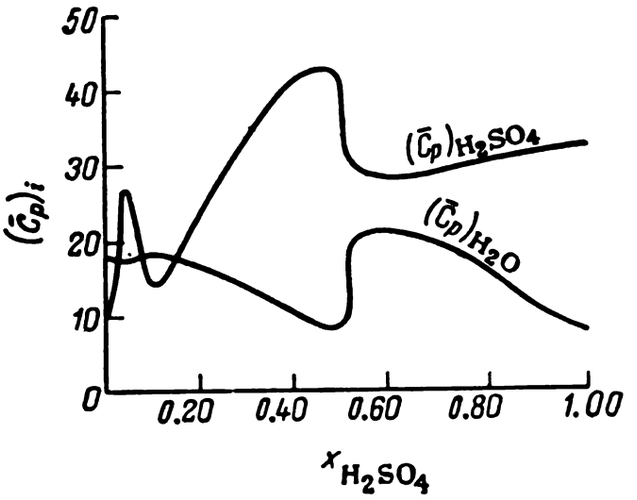

Fig. 71. Partial molar heat capacities of H_2O and H_2SO_4 in solutions of sulphuric acid (t = 15 °C)

Finally, we shall consider an equilibrium two-phase two-component system in which the temperature, pressure and composition undergo an infinitely small change. Here equilibrium is not violated, i.e.

$$d\bar{G}_1' = d\bar{G}_1'' \quad \text{and} \quad d\bar{G}_2' = d\bar{G}_2''$$

Expressing the composition of coexisting phases by the mole fraction of the second component, we get

$$\left.\begin{aligned}
&\left(\frac{\partial \bar{G}_1'}{\partial T}\right)_{p, x_2'} dT + \left(\frac{\partial \bar{G}_1'}{\partial p}\right)_{T, x_2'} dp + \left(\frac{\partial \bar{G}_1'}{\partial x_2'}\right)_{p, T} dx_2' = \\
&\quad = \left(\frac{\partial \bar{G}_1''}{\partial T}\right)_{p, x_2''} dT + \left(\frac{\partial \bar{G}_1''}{\partial p}\right)_{T, x_2''} dp + \left(\frac{\partial \bar{G}_1''}{\partial x_2''}\right)_{p, T} dx_2'' \\
\text{and} \\
&\left(\frac{\partial \bar{G}_2'}{\partial T}\right)_{p, x_2'} dT + \left(\frac{\partial \bar{G}_2'}{\partial p}\right)_{T, x_2'} dp + \left(\frac{\partial \bar{G}_2'}{\partial x_2'}\right)_{p, T} dx_2' = \\
&\quad = \left(\frac{\partial \bar{G}_2''}{\partial T}\right)_{p, x_2''} dT + \left(\frac{\partial \bar{G}_2''}{\partial p}\right)_{T, x_2''} dp + \left(\frac{\partial \bar{G}_2''}{\partial x_2''}\right)_{p, T} dx_2''
\end{aligned}\right\} \tag{8.19}$$

To transform these equations, we shall differentiate Eq. (8.13), written down for $Y = G$, two times with respect to x_2. We get

$$\frac{\partial^2 G}{\partial x_2^2} = -\frac{\partial \bar{G}_1}{\partial x_2} + \frac{\partial \bar{G}_2}{\partial x_2}$$

In accordance with Eq. (8.18) we have

$$\left(\frac{\partial \bar{G}_2}{\partial x_2}\right)_{p,T} = -\frac{x_1}{x_2}\left(\frac{\partial \bar{G}_1}{\partial x_2}\right)_{p,T}$$

It follows from these equations that

$$\left.\begin{aligned}\left(\frac{\partial \bar{G}_1}{\partial x_2}\right)_{p,T} &= -x_2\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{p,T}\\ \left(\frac{\partial \bar{G}_2}{\partial x_2}\right)_{p,T} &= x_1\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{p,T}\end{aligned}\right\} \tag{8.20}$$

Using the values of the corresponding derivatives found by means of Eqs. (8.6), (8.5) and (8.20) in Eq. (8.19), we get

$$\left.\begin{aligned}&(\bar{S}_1'-\bar{S}_1'')\,dT+(\bar{V}_1''-\bar{V}_1')\,dp - x_2''\frac{\partial^2 G''}{\partial x_2''^2}dx_2''+x_2'\frac{\partial^2 G'}{\partial x_2'^2}dx_2' = 0\\ &\text{and}\\ &(\bar{S}_2'-\bar{S}_2'')\,dT+(\bar{V}_2''-\bar{V}_2')\,dp + x_1''\frac{\partial^2 G''}{\partial x_2''^2}dx_2''-x_1'\frac{\partial^2 G'}{\partial x_2'^2}dx_2' = 0\end{aligned}\right\} \tag{8.21}$$

These equations will be used in the following for solving certain problems.

A. Storonkin (1948) generalized Eqs. (8.21) for multi-component two- and multi-phase systems. He applied the found equations to the solution of certain problems of the thermodynamic theory of multi-component systems both in the general form and for special cases (he considered changes in the pressure and temperature of coexisting phases depending on their composition in the greatest detail). The results of these investigations are combined in a monograph [B96].

Example 4. The density of an aqueous alcohol solution containing 60 weight % of CH_3OH is 0.8946 g/cm³, and the partial molar volume of the water in it is 16.8 cm³/mol. Find the partial molar volume of the alcohol in this solution.

Solution. The total volume of one mole of solution is

$$\frac{0.5424 \times 18 + 0.4576 \times 32}{0.8946} = 27.3$$

Hence $27.3 = 16.8 \times 0.5425 + \bar{V}_{alc} \times 0.4576$, whence $\bar{V}_{alc} = 39.8$ cm³.

8.2.2. Methods of Calculation

If the relationship $Y_{tot} = \varphi(n_i)$ is known, then $\bar{Y}_i$ is determined by differentiating Y_{tot} with respect to n_i. Introducing the corresponding value of n_i into the equation obtained, we find $\bar{Y}_i$ for a solution of a given composition. This method is time-consuming;

the experimental data have to be processed with such a high accuracy that the equation obtained would correspond to them within the entire range of compositions studied.

We shall consider two graphical methods. If we know the properties of solutions (for example the volumes containing different numbers of moles n_2 in the same amount of solvent), then by plotting a graph $Y_{tot} = \varphi(n_2)$ we get a curve whose slope at any point, i.e. for a solution of any composition, gives $\bar{Y}_2$. The shortcomings of this method include its comparatively low accuracy, the time-consuming calculations needed to convert mass concentrations into molar ones, and the impossibility of finding directly the partial molar quantities for both components.

The **slope-intercept method** allows us to simultaneously find $\bar{Y}_1$ and $\bar{Y}_2$: the property of a given solution is plotted on a graph as a function of the composition (Fig. 72 *). A tangent is drawn to the curve at the point corresponding to the given composition. Its intercepts on the ordinates $x_1 = 1$ and $x_2 = 1$ give, respectively, the partial molar quantities for the first and second components at the composition corresponding to the point of tangency.

Since $ab = ac - co \tan < cob$, then to prove that $ab = \bar{Y}_1$ (or $\bar{V}_1$ in the given case), we must show that

$$\bar{Y}_1 = Y - x_2 \frac{\partial Y}{\partial x_2} \qquad (8.22)$$

Seeing that the composition of a solution is an intensive property, we can change it in several ways. For this case, it is most convenient to change the composition without changing n_2, so that x_2 depends only on n_1. Since $Y = Y_{tot}/(n_1 + n_2)$, then

$$dY = \frac{dY_{tot}}{n_1 + n_2} - Y_{tot} \frac{dn_1}{(n_1 + n_2)^2}$$

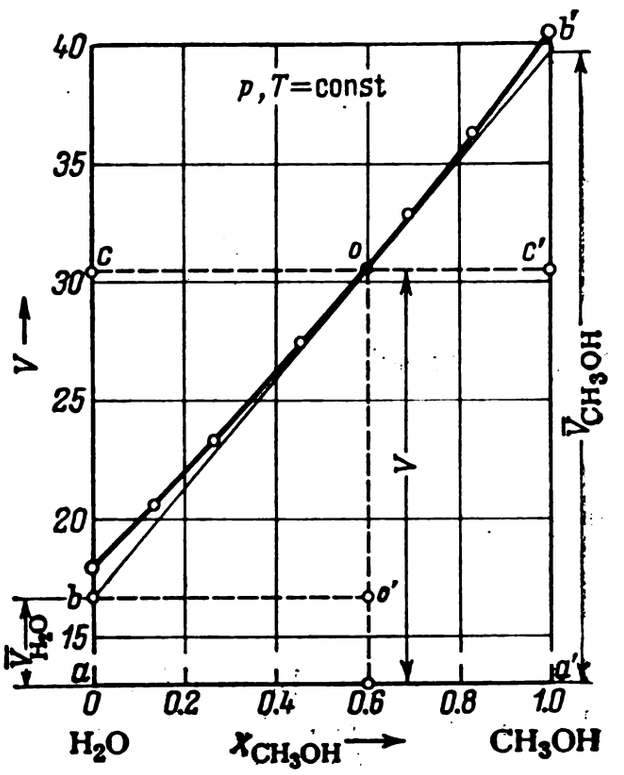

Fig. 72. Determination of partial molar quantities by slope-intercept method.
(See Example 6)

* If limited solubility were observed (for example when one of the components is a solid), then the curve $Y = \varphi(x_2)$ would obviously break off at a point corresponding to the concentration of a saturated solution.

and

$$dx_2 = -n_2 \frac{dn_1}{(n_1 + n_2)^2}$$

whence

$$\bar{Y}_1 = Y + x_2 \left[\frac{dY_{tot}(n_1+n_2)}{n_2 dn_1} - \frac{Y_{tot}}{n_2} \right] = Y + \frac{\partial Y_{tot}}{\partial n_1} -$$

$$- \frac{Y_{tot}}{n_1 + n_2} = Y + \bar{Y}_1 - Y$$

Q.E.D.

In the same way, we can prove that $a'b' = \bar{Y}_2$ (or $\bar{V}_2$ in the given case).

Equation (8.12) (for a binary solution) follows directly from the fact that *bob'* is a straight line. Examination of Fig. 72 shows that if one of the partial molar quantities grows with increasing concentration, then the other diminishes, and that

$$\lim_{x_1 \to 0} \bar{Y}_1 = Y_1^\circ$$

whereas

$$\lim_{x_1 \to 0} \bar{Y}_2 = \text{const}_1 \ (\neq Y_2^\circ)$$

and, conversely,

$$\lim_{x_2 \to 0} \bar{Y}_2 = Y_2^\circ$$

whereas

$$\lim_{x_2 \to 0} \bar{Y}_1 = \text{const}_2 \ (\neq Y_1^\circ)$$

Figure 72 can be used to substantiate Eq. (8.17) for a binary solution. Mentally displace point *o* in either direction over an infinitely small distance. This will correspond to an infinitely small change in the composition of the solution. The partial molar quantities will receive the increments $d\bar{Y}_1$ and $d\bar{Y}_2$ that are opposite in sign. Since the points are very close to one another, the lengths of the tangents from the points of tangency to the corresponding ordinates can be taken as the radii r_1 and r_2, and the lengths $d\bar{Y}_1$ and $d\bar{Y}_2$ as the arcs corresponding to these radii. But the arcs are proportional to the radii, i.e. $r_1 : r_2 = -d\bar{Y}_1 : d\bar{Y}_2$, while from the

similarity of the triangles it follows that $r_1 : r_2 = x_2 : x_1$. Combining the last two equations, we get $x_1 d\bar{Y}_1 + x_2 d\bar{Y}_2 = 0$.

Example 5. For the system H_2O-NaCl we have

$$V_{tot} = 55.51V_w + 16.4n_{salt} + 2.5n_{salt}^2 - 1.2n_{salt}^3$$

Find the partial and apparent molar volumes of sodium chloride in its half-molal aqueous solution.

Solution. In accordance with Eq. (8.4), we have

$$\bar{V}_{salt} = 16.4 + 5n_{salt} - 3.6n_{salt}^2$$

For $m = 0.5$ the value of $\bar{V}_{salt} = 18.0$ cm³.

Since at $m = 0.5$ we have $V_{tot} = 1008.675$, then by Eq. (8.10)

$$\Phi_{V_2} = \frac{1008.675 - 1000}{0.5} = 17.35$$

Example 6. Below are given the densities of aqueous solutions of methyl alcohol at $t = 20$ °C :

$[CH_3OH]$, weight %	0	20	40	60	80	90	100
ρ, g/cm³	0.9982	0.9666	0.9345	0.8946	0.8469	0.8202	0.7917

Use the slope-intercept method to calculate $\bar{V}_w$ and $\bar{V}_{alc}$ for the above concentrations.

Solution. We convert the densities into unit volumes, and then by Eq. (8.3) into molar volumes, and plot a graph of $V = \varphi(x_{alc})$ (see Fig. 72). Next, drawing tangents to the curve at the points corresponding to the indicated concentrations, we find $\bar{V}_w$ and $\bar{V}_{alc}$ (Fig. 72 shows the determination of $\bar{V}_w$ and $\bar{V}_{alc}$ for $x_{alc} = 0.60$). The intermediate and final results are given below :

$[CH_3OH]$, weight %	V, cm³/g	M_{av}	V, cm³/mol	$\bar{V}_w$	$\bar{V}_{alc}$
20	1.035	19.8	20.4	18.0	37.8
40	1.070	21.8	23.3	17.5	39.0
60	1.118	24.4	27.3	16.8	39.8
80	1.181	27.8	32.7	15.4	40.4
90	1.219	29.7	36.3	15.0	40.5

The calculations show that the mixing of the alcohol with water is attended by a decrease in volume. This can also be seen from Fig. 72 — the curve $V = \varphi(x_2)$ is convex toward the axis of abscissas.

8.3. HEAT CAPACITIES AND ENTHALPIES OF SOLUTIONS

8.3.1. Partial Molar Heat Capacities

The quantity $(\bar{C}_p)_i$, by Eq. (8.4), is determined by the equation

$$(\bar{C}_p)_i = \left[\frac{(\partial C_p)_{tot}}{\partial n_i}\right]_{p,\ T,\ n_j} \tag{8.23}$$

Experiments show that the partial molar heat capacities may be either positive or negative. In the latter case, the curve $Y = \varphi(x_i)$ deviates so greatly from a straight line that the tangent intercepts the axis $x_2 = 1$ below the axis of abscissas. Negative values of $(\bar{C}_p)_2$ are observed for some aqueous solutions of electrolytes and are probably connected with considerable hydration of the ions (the values of $\bar{V}_2$ may also be negative for the same reason).

Equation (8.10) when applied to aqueous solutions gives

$$(\bar{C}_p)_2 = \frac{(\partial C_p)_{tot}}{\partial m} = m\frac{\partial \Phi_C}{\partial m} + \Phi_C$$

or

$$(\bar{C}_p)_2 = \frac{\sqrt{m}}{2}\frac{d\Phi_C}{d\sqrt{m}} + \Phi_C \tag{8.24}$$

This equation permits us to find $(\bar{C}_p)_2$ from a graph of $\Phi_C = \varphi(\sqrt{m})$. Combining Eq. (8.24) with Eqs. (8.10) and (8.14) written down for the heat capacity, we get

$$(\bar{C}_p)_1 - (\bar{C}_p^\circ)_1 = -\frac{m}{55.51}\left(\frac{\sqrt{m}}{2}\frac{d\Phi_C}{d\sqrt{m}}\right) \tag{8.25}$$

Thus, using the result of measuring the total heat capacity of a solution C_p (i.e. 1000 g of H_2O + m mol of solute), we can calculate Φ_C, $(\bar{C}_p)_2$ and $(\bar{C}_p)_1 - (\bar{C}_p^\circ)_1$.

We can consider for solutions of electrolytes (F. Rossini) that

$$\Phi_C = \Phi_C^* + A\sqrt{m} \tag{8.26}$$

where

$$\Phi_C^* = \Phi_C^\circ = (\bar{C}_p^\circ)_2$$

Combining Eq. (8.26) with Eqs. (8.24) and (8.25), we have

$$(\bar{C}_p)_2 = (\bar{C}_p^\circ)_2 + \frac{3}{2}A\sqrt{m} \tag{8.27}$$

and

$$(\bar{C}_p)_1 - (\bar{C}_p^\circ)_1 = -\frac{A}{2 \times 55.51}m^{\frac{3}{2}} \tag{8.28}$$

The last two equations make it possible to find the constants $(\bar{C}_p^\circ)_1$ and A according to two values of $C_p = \varphi(m)$ and thus solve the problem of calculating the heat capacities of the components of a solution.

Example 7. Use the experimental data on the heat capacities of aqueous solutions of HCl ($t = 25\,°C$) given below to calculate the apparent and partial molar heat capacities of HCl and the relative partial molar heat capacities of H_2O in solutions having the indicated concentrations:

m	0.1	0.5	1	1.5	2
C_p, cal per (55.51 + m) mol of solution	996.965	986.02	974.31	964.045	954.98

Solution. We calculate Φ_C ($\bar{C}_p^\circ = 18$) by Eq. (8.10), next we compute the values of $\sqrt{m}$ and plot a graph of Φ_C against $\sqrt{m}$ (Fig. 73). From the graph, in accordance with Eq. (8.26), we find the heat capacity of HCl in an infinitely dilute solution $\Phi_C^* = C_p^* = -32.7$ and $[d\Phi_C/d(\sqrt{m})] = 7.25$.

The values of $(\bar{C}_p)_2$ calculated by Eq. (8.24) or (8.27) are also plotted on Fig. 73. Finally, by Eq. (8.25) or (8.28) we determine $(\bar{C}_p)_1 - (\bar{C}_p^\circ)_1$. The equations used for the calculations have the form

$$(\Phi_C)_{HCl} = -32.7 + 7.25\sqrt{m}$$

$$(\bar{C}_p)_{HCl} = -32.7 + 10.7\sqrt{m}$$

$$(\bar{C}_p)_{H_2O} - (\bar{C}_p^\circ)_{H_2O} = -0.0652 m^{\frac{3}{2}}$$

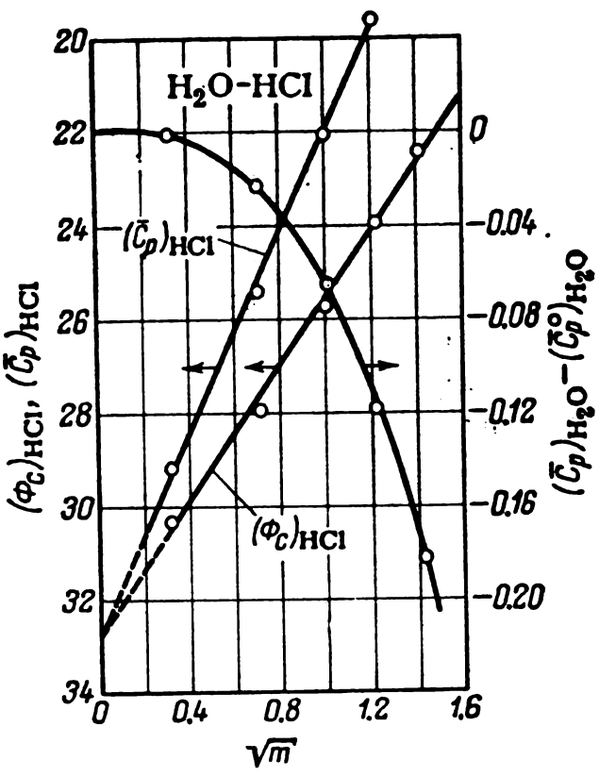

Fig. 73. Apparent and partial molar heat capacities of HCl in aqueous solutions ($t = 25\,°C$).
(See Example 7)

8.3.2. Partial Molar Enthalpies

In accordance with Eq. (8.4), we have

$$\bar{H}_i = \left(\frac{\partial H_{tot}}{\partial n_i}\right)_{p,\,T,\,n_j}$$

An isobaric change in $\bar{H}_i$ with temperature is expressed by the equation

$$\left(\frac{\partial \bar{H}_i}{\partial T}\right)_p = \frac{\partial}{\partial T}\left(\frac{\partial H_{tot}}{\partial n_i}\right)_{p,n_j} = \frac{\partial}{\partial n_i}\left(\frac{\partial H_{tot}}{\partial T}\right)_{p,n_j}$$

In connection with Eq. (8.23) we finally get

$$\left(\frac{\partial \overline{H}_i}{\partial T}\right)_{p,\ x} = (\overline{C}_p)_i \tag{8.29}$$

Differential and Integral Heats of Solution. If we dissolve one mole of a substance in an infinitely great amount of a solution, or, which is the same, if we add an infinitely small amount of the solute to a solution of the given concentration and reduce the results to one mole of the solute, then the heat effect is called the **differential** or **partial heat of solution.** If we dissolve one mole of a substance in such an amount of pure solvent that will give us a solution of the given composition, then the heat effect observed is called the **integral heat of solution.** Here, as previously (see Chap. 3), it is considered that the system has the same temperature before and after the process.

The values of the integral heat of solution of a number of substances are given in Table 11.

Table 11. **Integral Heats of Solution ΔH°_{298} (kcal/mol) of Selected Substances in Water**

Solute	n^*	ΔH°_{298}	Solute	n^*	ΔH°_{298}
Crystalline Substances			H_2O_2	∞	−0.84
			H_3PO_3	5 000	1.6
$AgNO_3$	∞	5.42	H_2SO_4	∞	−23.1
$AlCl_3$	∞	−78.12	H_3PO_4	400	−1.54
$Cd(ClO_4)_2$	∞	−27.00	$H_4P_2O_7$	∞	−3.7
$CuCl_2$	∞	−12.36	$SnCl_4$	∞	−33.94
$FeCl_3$	1 000	−31.64	*Gases*		
H_3BO_3	∞	5.21			
NH_4Cl	∞	3.53	CH_4	40 000	−3.14
NH_4HCO_3	∞	9.85	CO	60 000	−2.62
NH_4HSO_4	∞	−4.26	CO_2	1 600	−4.72
NH_4NO_3	∞	6.14	Cl_2	1 000	6.4
$(NH_4)_2SO_4$	∞	1.10	HBr	∞	−20.35
$NiCl_2$	∞	−19.88	HCl	∞	−17.88
$ZnCl_2$	∞	−17.40	HF	∞	−14.5
$ZnSO_4$	∞	−19.90	HI	∞	−19.57
Liquids			H_2S	1 500	−4.6
			NH_3	100 000	−8.02
CH_3COOH	∞	−0.37	SO_2	7 000	−9.73
C_2H_5OH	∞	−2.39	SO_3	1	−31.7
HNO_3	∞	−7.95			

* Number of moles of H_2O per mole of solute.

The heats of solution of strong electrolytes in an infinitely great amount of water can be found in accordance with Hess's law by subtracting the heat of formation of the compound from the sum of the values of the standard heats of formation of the corresponding ions (Appendix 2). Inspection of Table 11 shows that the order of magnitude of the heats of solution of many substances and of the heats of chemical reactions (the heats of formation) coincides.

Figure 74 compares the values of the integral heats of solution for various similar systems (two series of salts-analogues in the same solvent, one series of analogues in related solvents, and two similar substances in the same solvent, respectively). We can recommend such approximate regularities, serving as examples of the methods of comparative calculations [B45], for an assessment of the values of the heats of solution.

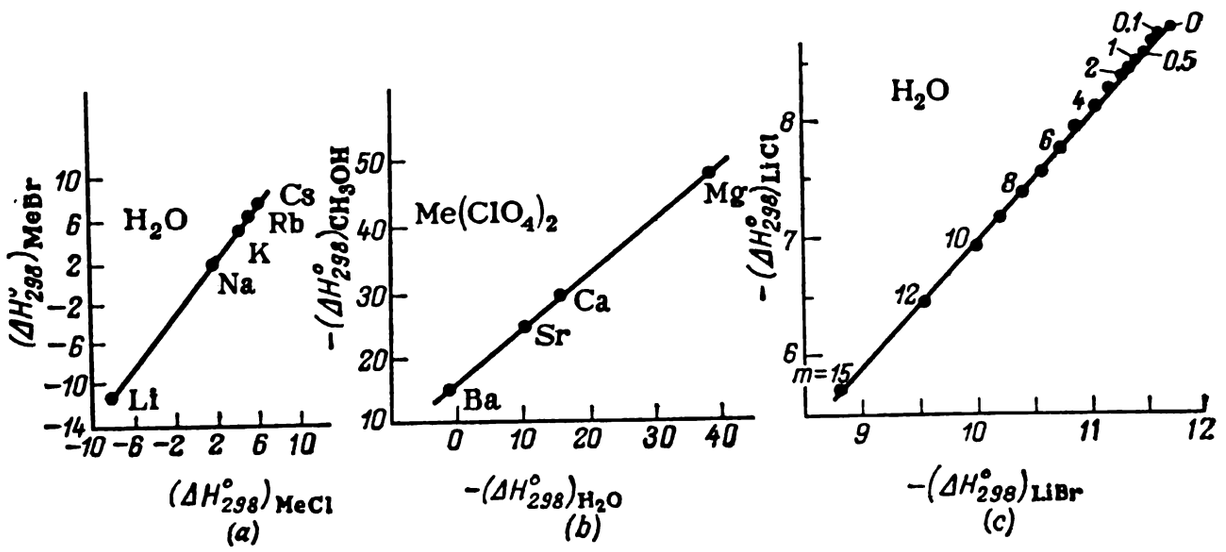

Fig. 74. Relationship between integral heats of solution:
a — alkali metal chlorides and bromides in water; *b* — perchlorates of beryllium subgroup elements in water and methanol; *c* — lithium bromides and chlorides in water for equal concentrations

A general picture of the change in the heats of solution of related substances is shown in Fig. 75. Even if we take into consideration the incompleteness of the data, the low accuracy of some of the values, and the availability of data for some of the elements only on chlorides with a lower degree of oxidation than the maximum possible one, the periodic nature of the graph is doubtless.

The values of the integral and differential heats of solution may differ appreciably. The discrepancies between them are especially great for concentrated solutions, when they may fail to coincide not only in value, but also in sign. Lowering of the concentration is attended by diminishing of the difference between the two quantities, and for infinite dilution they become equal. The heat of solution in an infinitely dilute solution (or in a pure solvent) is called the **first** heat in contrast to the **last** heat — the name given to the differential heat of solution in a saturated solution.

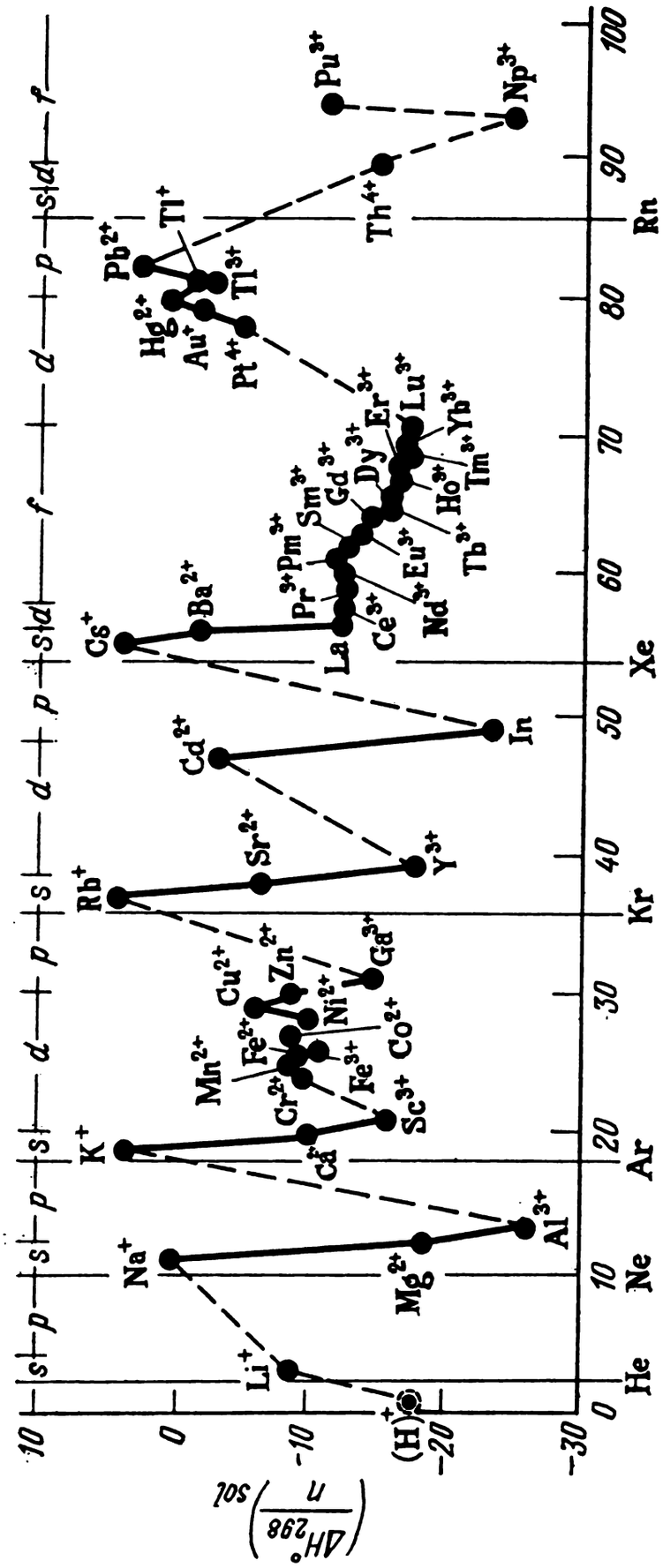

Fig. 75. Dependence of the standard heat of solution $(\Delta H^\circ_{298}/n)_{sol}$ (in kcal/g-equiv) of chlorides on the atomic number Z of an element ($n_{H_2O} = \infty$)

The differential heat of solution is mainly used in thermodynamic calculations (see below).

Assume that dn_2 moles of the solute are added to a solution consisting of n_1 moles of the solvent and n_2 moles of the solute at p, T = const. The heat effect of this process is

$$\left[H_{tot} + \left(\frac{\partial H_{tot}}{\partial n_2}\right)_{p,\,T,\,n_1} dn_2\right] - \left[H_{tot} + (H_2^\circ)^c\, dn_2\right]$$

where H_{tot} = enthalpy of the solution before mixing
$(H_2^\circ)^c$ = molar enthalpy of the pure solute.

We can obtain an equation determining the heat of dilution in a similar way. By relating the values obtained to one mole of the added substance, i.e. by dividing them by dn_2 (or dn_1), respectively, we find the value of the differential heat of solution (dilution)

$$\frac{\delta Q}{\partial n_i} = \bar{H}_i - H_i^\circ \qquad (8.30)$$

The relative enthalpy of a substance $\bar{L}_i$ is often used. It is the difference between $\bar{H}_i$ and the molar enthalpy of a given component in the standard state—an infinitely dilute solution.* Hence Eq. (8.30) becomes

$$\frac{\delta Q}{\partial n_2} = \bar{L}_2 - L_2 \quad \text{and} \quad \frac{\delta Q}{\partial n_1} = \bar{L}_1 \qquad (8.31)$$

Equations (8.30) and (8.31) are illustrated by Fig. 76, which shows a graphical method of finding $\bar{L}_1$ and $\bar{L}_2$ (for $x_{SO_3} = 0.25$).

The relationship between $\bar{L}_1$ and $\bar{L}_2$ is expressed by Eq. (8.18). Its integration for the given case makes it possible to compute $\bar{L}_2$ according to $\bar{L}_1$ or, conversely, $\bar{L}_1$ according to $\bar{L}_2$ (integration is performed graphically).

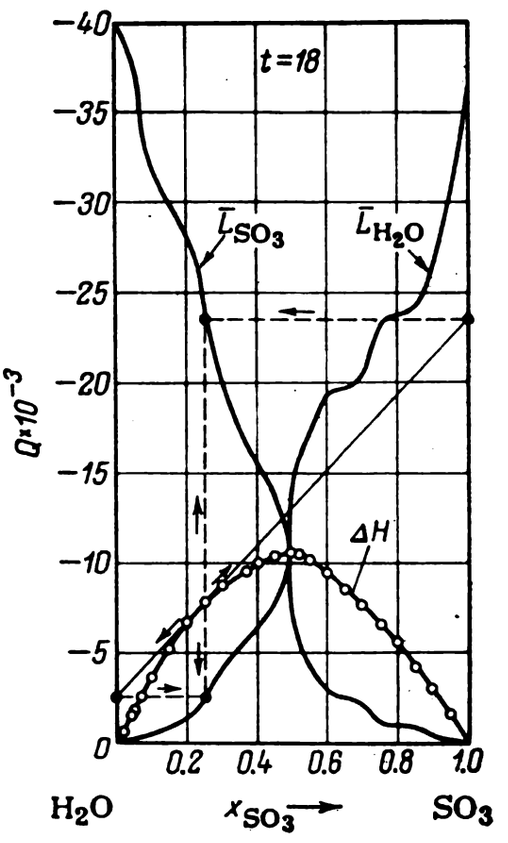

Fig. 76. Integral and differential heats of solution and dilution in the system H_2O-SO_3.
(See Example 8)

* The choice of this standard state (instead of that of pure components) is especially convenient for the solute, because if we know the values of the heat of dilution, but have no data on the heat of solution, there is no way in calculations for changing from the state of the pure solute to that of a solution. This choice has an advantage over the assumption that the enthalpy in the initial state equals zero, since the latter is possible only at a definite temperature.

K. Mishchenko and his assistants conducted extensive investigations of the heats of solution and hydration.

If data are available on the heat of dilution of solutions (of substance A) having two concentrations to infinite dilution, then on the basis of Hess's law, the heat of transition from one concentration to the other is determined by the difference between the first two quantities.

For the process

$$A \cdot n\mathrm{H_2O} + (n_\infty - n)\mathrm{H_2O} = A \cdot n_\infty \mathrm{H_2O} = A(\mathrm{aq})$$

the heat effect

$$\Delta H = \bar{H}_2^\circ + n_\infty \bar{H}_1^\circ - (n_\infty \bar{H}_1^\circ - n_1 \bar{H}_1^\circ + \bar{H}_2 + n_1 \bar{H}_1) = \bar{H}_2^\circ - \bar{H}_2 + n_1(\bar{H}_1^\circ - \bar{H}_1) \qquad (8.32)$$

which in accordance with Eq. (8.10) gives

$$-\Delta H = \Phi_H - \Phi_H^\circ$$

or

$$m(\Phi_H - \Phi_H^\circ) = m(\bar{H}_2 - \bar{H}_2^\circ) + 55.51(\bar{H}_1 - \bar{H}_1^\circ) \qquad (8.33)$$

Differentiating Eq. (8.33) with respect to m and taking Eq. (8.17) into account, we get

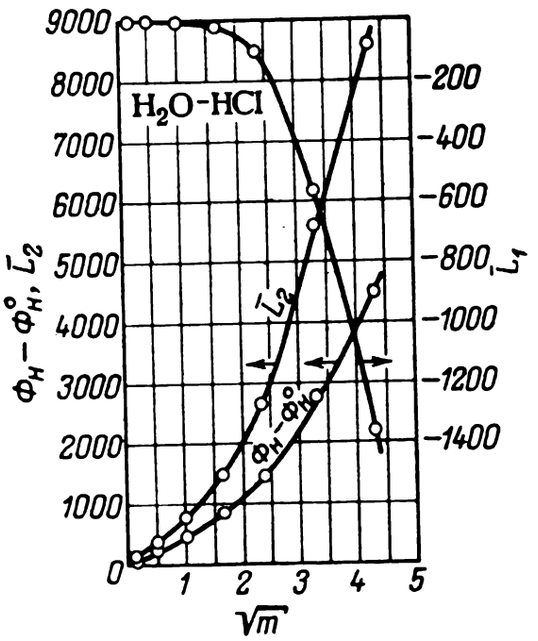

Fig. 77. Apparent enthalpies of HCl and heats of solution and dilution in the system H_2O-HCl.
(See Example 9)

$$\bar{H}_2 - \bar{H}_2^\circ = \Phi_H - \Phi_H^\circ + m\frac{d(\Phi_H - \Phi_H^\circ)}{dm}$$

or after substitution

$$\bar{H}_2 - \bar{H}_2^\circ = \bar{L}_2 = \Phi_H - \Phi_H^\circ + \frac{\sqrt{m}}{2}\frac{d(\Phi_H - \Phi_H^\circ)}{d\sqrt{m}} \qquad (8.34)$$

Combining Eqs. (8.34) and (8.33), we find

$$\bar{H}_1 - \bar{H}_1^\circ = \bar{L}_1 = -\frac{m}{55.51}\frac{\sqrt{m}}{2}\frac{d(\Phi_H - \Phi_H^\circ)}{d\sqrt{m}} \qquad (8.35)$$

Calculations are performed on the basis of values of $\Phi_H - \Phi_H^\circ$ obtained by extrapolation of the heat of dilution to infinite dilution; $\bar{L}_2$ and then $\bar{L}_1$ are calculated with the aid of a graph of $\Phi_H - \Phi_H^\circ$ against $\sqrt{m}$ (Fig. 77).

The changes in the differential heats of solution and dilution with a change in temperature with a view to Eqs. (8.23) and (3.11) equal, respectively,

$$\frac{\partial(\overline{H}_2 - H_2^c)}{\partial T} = (\overline{C}_p)_2 - (C_p)_2^c \quad \text{and} \quad \frac{\partial(\overline{H}_1 - \overline{H}_1^\circ)}{\partial T} = (\overline{C}_p)_1 - (\overline{C}_p^\circ)_1$$

Example 8. Using the values of the integral heat of formation of H_2SO_4 from H_2O and SO_3 given in Fig. 76, find the amount of heat (1) liberated when such an amount of water is added to 100 kg of 29% oleum (the per cent of free SO_3) as to obtain a 64.4% aqueous solution of H_2SO_4; (2) which should be removed in the process of adding 29% oleum to 100 kg of a 40.5% solution of H_2SO_4 until a content of 96.1% of H_2SO_4 is obtained.

Solution. 1. The mole fraction of SO_3 in oleum is

$$\left(\frac{29}{80} + \frac{71}{98}\right) \Big/ \left(\frac{29}{80} + \frac{71}{98} + \frac{71}{98}\right) = \frac{1.088}{1.813} = 0.60$$

and in the solution obtained it is

$$\frac{64.4}{98} \Big/ \left(\frac{64.4}{80} + \frac{35.6}{18} + \frac{64.4}{98}\right) = 0.20$$

The total number of moles of oleum equals 1.813, and of the solution obtained 0.60/0.20 = 3. Since according to Hess's law, the required quantity equals the difference between the value of the heat of solution of the initial and final solutions, then using these values (see Fig. 76), we find that $3 \times 6600 - 1.813 \times 9400 = -2760$ kcal will be liberated during the mixing.

2. The number of moles of the initial solution equals

$$\frac{40.5}{98} + \frac{40.5}{98} + \frac{59.5}{18} = 4.133$$

olutions	1	2	3
$[H_2SO_4]$, weight %	40.5	oleum	96.1
Mole fraction of SO_3	0.10	0.60	0.40
Integral heat of solution (see Fig. 76)	−3600	−9400	−10 000

We find the number of moles of oleum added from the equation of the material balance $4.133 \times 0.10 + n \times 0.60 = (n + 4.133)\,0.40$, whence $n = 6.2$ (kg·mol).

In accordance with Hess's law, the required heat effect

$$\Delta H = \Delta H_3 - (\Delta H_1 - \Delta H_2)$$

or

$$\Delta H = 10\,000\,(4.133 + 6.2) - (3600 \times 4.133 + 9400 \times 6.2) = \\ = 30\,170 \text{ kcal}$$

Example 9. The heat of solution of HCl in H_2O at $t = 25\,^\circ C$ can be represented by the following values of the relative apparent enthalpies of HCl in aqueous solutions

Composition of solution, mol H_2O/mol HCl	3	5	10	20	50	200	1600
$\Phi_H - \Phi_H^\circ$, cal/mol HCl	4470	2760	1460	850	482	249	90

Determine: (1) the relative molar enthalpies of the components in the solutions indicated above; (2) the value of the heat of dilution of a solution containing one mole of HCl in 15 moles of H_2O up to infinite dilution.

Solution. 1. After converting the composition to molality, we plot the above data on a graph in the coordinates $\Phi_H - \Phi_H^\circ$ against $\sqrt{m}$ (see Fig. 77). Next we draw tangents to the curve (for various values of $\sqrt{m}$) and by Eqs. (8.34) and (8.35) we calculate L_2 and L_1. The results of the calculations are given in Fig. 77.

2. The values of $m = 3.701$ and $\sqrt{m} = 1.924$ correspond to the solution $HCl \cdot 15H_2O$. In Fig. 77, we find $\Phi_H - \Phi_H^\circ = 1050$; consequently, the process of dilution is connected with the liberation of 1050 cal.

8.4. IDEAL SOLUTIONS

The interaction between different and like molecules of the components of an ideal solution is the same (all the molecules have the same force fields). Therefore, when part of a component is replaced with another one, the ability of each of them to pass over into the gaseous phase will not change. But since this tendency, expressed by the fugacity of the component, is the more considerable, the greater is the relative content of its molecules in the liquid, then the fugacity of the component over an ideal solution should be proportional to its mole fraction in the solution, i.e. $f_i^g = \text{const } x_i^{lq}$. The proportionality factor is determined from the initial condition $x_i^{lq} = 1$; const $= f_i^\circ$, i.e. it equals the fugacity of the pure component. The equality of the fugacities of a component of a solution in two coexisting phases allows us to arrive at the final formulation of a law that is one of the criteria of the ideal nature of a solution: *the fugacity of a component of an ideal solution equals the fugacity of the pure component multiplied by its mole fraction*, i.e.

$$f_i = f_i^\circ x_i \qquad (8.36)$$

The quantity f_i° is constant for given p and T. It equals the fugacity of the pure component at a pressure equal to the total pressure over the solution. If the standard state of the component is taken the same as for the pure substance (at the same pressure and temperature), then in accordance with the definition of activity Eq. (8.36) becomes

$$a_i = x_i \quad \text{or} \quad \gamma_i = \frac{a_i}{x_i} = 1 \tag{8.37}$$

The failure of the **activity coefficient** γ_i (see Chap. 12) to coincide with unity is a measure of the deviation of a solution from an ideal one, in the same way as the deviation of f/p from unity is a measure of the deviation of the properties of a pure gas from those of an ideal gas (see Chap. 6).

Equation (8.36) is the **generalized Raoult's law.** It holds for the region of concentrations in which a solution remains ideal and the pure components are stable at the pressure and temperature of the mixture.

It follows from a comparison of Eq. (8.36) and Eqs. (6.32) and (8.7) that

$$\overline{V}_i = V_i^\circ \tag{8.38}$$

From Eqs. (8.8), (8.36) and (6.39) we get

$$\overline{H}_i = H_i^\circ \tag{8.39}$$

Consequently, we can also write down that

$$(\overline{C}_p)_i = (C_p^\circ)_i \tag{8.40}$$

i.e. the volumes, enthalpies (and heat capacities) are additive and do not depend on the composition. We thus reach the following important conclusion: *when an ideal solution is formed, no change in the volume occurs* ($\Delta V = 0$), *and no heat effect is observed* ($\Delta H = 0$). The essential conditions here include not only identical pressure (over the solution and over each of the pure substances) and identical temperatures, but also an identical state of aggregation of the components and the solution.

If the above quantities were not additive, the fugacities of the components of an ideal solution would be proportional to the mole fractions at one temperature and pressure, but would not be proportional to them at other values of x, p and T.

Here we must draw attention to two circumstances.

1. A given solution can be considered ideal only when Eqs. (8.36), (8.38) and (8.39) hold *simultaneously*.

2. It is easier to verify Eqs. (8.38) and (8.39) experimentally than Eq. (8.40). If any of them holds for a solution of a *certain* composition, this cannot be a criterion of the ideal nature of the solution, because both the volume and the heat effect may change for other

concentrations. If a solution is ideal at all concentrations, a graph plotted in the coordinates volume (enthalpy, heat capacity) against concentration (see Fig. 72) will be a straight line, because the equations of the additivity of the partial molar volumes (enthalpies, heat capacities) [Eq. (8.14)] will transform into equations of the additivity of the corresponding molar quantities for an ideal solution. Cases are known, however, when the line characterizing, for instance, the change in volume is a curve intersecting the straight line for an ideal solution, i.e. only at one point do we have $\overline{Y} = Y_i^\circ$ (where Y stands for V, H or C_p).

For liquid solutions at low pressures and at temperatures far from critical, the quantity f_i° in Eq. (8.36) may be considered equal to $(f_i^\circ)_{p_i^\circ}$ — the fugacity of a pure component at the pressure of its saturated vapour. Otherwise this simplification cannot be used, and recalculation is necessary by the equation

$$\ln \frac{(f_i^\circ)_p}{(f_i^\circ)_{p_i^\circ}} = \frac{1}{RT} \int_{p_i^\circ}^{p} V_i^\circ dp \qquad (8.41)$$

obtained by integration of Eq. (8.7) (taking into account the fact that $\overline{V}_i = V_i^\circ$) within the limits from p_i° to the total pressure p over the solution.

Equation (8.36) can also be applied to solutions of gases. Indeed, if Eq. (8.38) holds for a component of a gas mixture, i.e. $\overline{V}_i = V_i^\circ$ (at the same p and T), then $\alpha_i = \alpha$ and Eq. (8.9) becomes

$$RT \ln f_i = RT \ln p + RT \ln x_i - \int_0^p \alpha \, dp$$

But the first and third terms of the right-hand side of this equation in accordance with Eq. (6.42) equal $RT \ln f_i^\circ$, i.e. Eq. (8.9) transforms into Eq. (8.36).

The possibility of using Eq. (8.36) for gas mixtures has great practical significance, because owing to the very small amount of data on the relationship $\overline{V}_i = \varphi(p, T, x)$, Eq. (8.9) finds practically no application.

An analysis of experimental data shows that for comparatively low pressures (of the order of scores of atmospheres) Eq. (8.36) is accurate for gas mixtures of any composition. For many mixtures, it is also sufficiently satisfactory for greater pressures (especially for mixtures whose components have close compressibilities), although it gives somewhat smaller values of f_i than Eq. (8.9), which can be applied to any gas mixtures in any conditions.

Attention should be given to the fact that when Eq. (8.36) is applied to the gaseous phase, the fugacity of a pure component is *always* taken for the *total* pressure of the mixture. Therefore, Raoult's law when applied to a gas mixture is also called the **fugacity rule.**

This rule takes into account not only the deviation of the properties of a mixture from the laws for an ideal gas, but also the influence of the pressure on the properties of the pure components. When a mixture follows the laws of ideal gases, Eq. (8.36) transforms into Eq. (6.14), because the fugacity of a component may be replaced by its partial pressure, and the fugacity of the pure component f_i° at a pressure equal to the total pressure in the mixture may be simply replaced by the total pressure.

It is obvious from the above that the concepts "mixture of ideal gases" and "ideal gas mixture" are not equivalent. The former simultaneously obeys Eqs. (6.14) and (6.16), while the latter obeys Eq. (8.36) and, therefore, also the fugacity rule. In other words, a compressed gas mixture, not being a mixture of ideal gases, may nevertheless be an ideal gas mixture.

If a gas mixture is a solution of the vapour of a condensed phase in a compressed gas, then the quantity x_i in Eq. (8.36) will correspond to the solubility of the liquid (solid) substance in the compressed gas. However, for solutions, the molecules of whose components have sharply differing force fields, for example besides nonpolar substances they contain polar ones, the additivity of the volumes is not observed, i.e. such solutions are not ideal. Consequently, calculation of the solubility by Eq. (8.36) leads to a discrepancy with experimental data — notwithstanding this equation, the solubility expressed as a mole fraction depends on the nature of the solvent. Hence, the dependence of the concentration of water vapour on the nature of the compressed gas noted in Sec. 7.5 is a result of the fact that the solutions formed are not ideal (see also Sec. 9.3).

When a substance passes into an ideal solution where its mole fraction is x_i, the change in the Gibbs energy in accordance with Eq. (8.36) is

$$\overline{G}_i - G_i^\circ = RT \ln \frac{f_i}{f_i^\circ} = RT \ln a_i = RT \ln \frac{f_i^\circ x_i^{lq}}{f_i^\circ} = RT \ln x_i^{lq}$$

or

$$\mu_i = \mu_i^\circ(p, T) + RT \ln x_i^{lq} \qquad (8.42)$$

Since $x_i^{lq} < 1$, then $\overline{G}_i \neq G_i^\circ$, i.e. in an ideal solution the Gibbs energies (and therefore the entropies) are not additive. In accordance with Eq. (8.42), the Gibbs energy of a solution is less than the summary Gibbs energy of the components (otherwise the process of solution would not be spontaneous).

Upon an infinitely small change in the composition, the partial molar Gibbs energy of a component of a solution in accordance with Eq. (8.42) will change by the quantity

$$d\bar{G}_i = RT\, d \ln f_i = RT\, d \ln x_i \tag{8.43}$$

i.e.

$$\left(\frac{\partial \bar{G}_i}{\partial x_i}\right)_{p,\, T,\, n_j} = \frac{RT}{x_i} \tag{8.44}$$

It follows from Eq. (8.42) that the properties of the chemical potential depend on the properties of the given component and on those of the other components. For an ideal solution, it makes absolutely no difference what substances form the solution and what properties they have. The value of the chemical potential of the given component depends only on the relative amounts of the other substances and only inasmuch as this causes the mole fraction of the given substance to change. Hence follows the "non-sensitivity" of the chemical potential to the properties of the other constituents, which, for instance in the case of a mixture of ideal gases, is expressed in that "each gas behaves in a mixture as if it were alone".

The application of Eq. (8.42) to the general laws holding for any solutions makes it possible to determine the thermodynamic properties of ideal solutions regardless of their state of aggregation. Indeed, the transition from a liquid to a gas can be accomplished without violating homogeneity by correspondingly changing p and T. Therefore, to state that Eq. (8.42) can be used as the basis of the thermodynamics of ideal solutions regardless of their state of aggregation, we must prove that the change in the Gibbs energy for an ideal solution does not depend on the change in p and T. At the same time in an ideal solution at all values of p and T, the change in V and H in accordance with Eqs. (8.38) and (8.39) equals zero, which in connection with the equations $(\partial \Delta G/\partial T)_p = -\Delta S$ and $(\partial \Delta G/\partial p)_T = \Delta V$ following from Eqs. (5.24) and (5.25) results, first, in the change in the Gibbs energy not depending on the pressure when a pure component is added, and, second, in the change in the Gibbs energy related to the temperature not depending on the temperature.

If the vapour over a liquid solution can be considered as a mixture of ideal gases, then Eq. (8.36) acquires the following form:

$$p_i = p_i^\circ x_i^{\text{liq}} \tag{8.45}$$

i.e. *the partial vapour pressure of a given component over a solution equals the saturated vapour pressure over the pure component (at the given temperature) multiplied by the mole fraction of this component in the liquid phase.*

Equation (8.45) is the mathematical formulation of Raoult's law in the form which he proposed (1886). This equation is usually written as follows for a solution of a non-volatile substance in a volatile solvent:

$$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{n_2}{n_2 + n_1} \tag{8.46}$$

The diminishing of the vapour pressure over a solution of a *non-volatile* substance in comparison with the pure solvent (at the same temperature) is clear from the Le Chatelier principle: when a non-volatile substance, for example a salt, is introduced into the equilibrium system water-vapour, part of the vapour transforms into the liquid, resulting in a lower vapour pressure.

Ideal solutions are formed by substances similar in their chemical composition and physical properties. Deviations from the ideal state are due either to chemical effects (association, dissociation, solvation, etc.) or to physical effects (the influence of the difference in molar volumes and the forces of interaction between molecules). The former, as a rule, diminish with increasing temperature, whereas the deviations due to the difference in the size of the molecules grow.

To determine whether or not a component of a gas mixture follows the laws of an ideal solution, it is important to know how great its pressure is. For liquid solutions, the pressure (except when very high pressures and temperatures close to the critical ones are used) is of no practical significance, and other factors come to the foreground. This is the reason why liquid solutions, in contrast to their gas counterparts, are not ideal at ordinary pressures.

The introduction of the concept "ideal solution" is important in practice as well as in theory. Strictly speaking, no real solution except for optically active isomers and mixtures consisting of components that differ in their isotope composition has the properties of an ideal solution. Very many solutions, however, behave practically like ideal ones. In view of the simple nature of the laws which ideal solutions obey and the complications and even impossibility of calculating the properties of real solutions, we often have to tolerate a deliberate inaccuracy and consider a solution to be ideal. Therefore, the theory of ideal solutions makes it possible with a certain approximation to solve many problems connected with solutions in general.

In the following, using known relationships characterizing ideal solutions, we shall transform them into equations holding for any solution.

Example 10. A mixture containing 100 kg of benzene (C_6H_6) and toluene ($C_6H_5CH_3$) is taken at $t = 100\,^\circ C$. The partial pressures

of the benzene and toluene over the solution equal 656 and 286 mm Hg, respectively. Find the mass of each component, considering the liquid phase to be an ideal solution.

Solution. We find the vapour pressures of the pure components at $t = 100\,°C$ from a graph of $p = \varphi(T)$ (see Fig. 55). They are 1340 and 560 mm Hg, respectively. By Eq. (8.45) we get

$$x_{benz} = \frac{656}{1340} = 0.49 \quad \text{and} \quad x_{tol} = \frac{286}{560} = 0.51$$

Combining the equations

$$\frac{g_{benz}/78.1}{g_{benz}/78.1 + g_{tol}/92.1} = 0.49 \quad \text{and} \quad g_{benz} + g_{tol} = 100 \text{ kg}$$

we get

$$g_{benz} = 44.9 \text{ kg} \quad \text{and} \quad g_{tol} = 100 - 44.9 = 55.1 \text{ kg}$$

8.5. INFINITELY DILUTE SOLUTIONS

We have already noted that thermodynamic relationships which are faultless in their accuracy and hold for any solutions cannot be used in practice, because they need data which are not available at present. These relationships, in particular, include Eq. (8.21) covering all the thermodynamics of two-component systems. They have a simple and easily-used form for ideal solutions, but there are only a few solutions which approach ideal ones in their properties within a *broad* range of concentrations, if we exclude mixtures of gases at low pressures.

At the same time, there is a category of solutions for which the general thermodynamic relationships can be used in specific calculations. These are **infinitely dilute solutions,** i.e. solutions in which the content of the solute is very small in comparison with that of the solvent.*

The study of infinitely dilute solutions is not of purely theoretical interest. The properties that in principle are inherent only to these solutions also remain in force to a great extent for *finite* (sufficiently low) concentrations. Thus, aqueous solutions of H_2, N_2, CO, O_2,

* The general relationships can also be used to obtain numerical results for so-called **regular** solutions (their properties are considered in [B40]) and **athermic** solutions (many solutions of high-molecular compounds in conventional solvents are close to them). The former are characterized by the fact that for them ΔH_{mix} does not equal zero (and is proportional to the logarithm of the activity coefficient of the component), and $\Delta S_{mix} = \Delta S_{id}$; for the latter $\Delta H_{mix} = 0$, while the activity coefficient is determined only by the entropy term and does not depend on the temperature.

CH_4 and other gases behave like infinitely dilute ones; even at very high pressures, their solubility is negligibly small ($x_2 \approx 0.000\,02$ to 0.0007).

Thermodynamics cannot determine to what concentrations and with what degree of accuracy the behaviour of a solution corresponds to the laws of infinitely dilute solutions; this is determined experimentally. An analysis of experimental data shows that the limit of the concentrations for solutions of non-electrolytes can be taken equal to $x_2 \approx 0.01$ and in some cases even reaches $x_2 \approx 1$. For solutions of electrolytes, it sometimes lowers to $x_2 \approx 10^{-6}$.

The study of the properties of infinitely dilute solutions is of practical interest for still another reason: it is often necessary in calculations to extrapolate properties found experimentally from finite concentrations to very small ones. The importance of studying infinitely dilute solutions was indicated by D. Mendeleev.

It must be stressed that the thermodynamics of infinitely dilute solutions is entirely true for solutions whose pure solvent is not in its critical state. If this condition is not observed, appreciable correctives have to be introduced, because the limiting value of a number of quantities for critical infinitely dilute solutions depends on the path followed in approaching the limit. The thermodynamics of such solutions was developed in the research of I. Krichevsky and his assistants and was verified on the basis of extensive experimental data mainly obtained by them.

8.5.1. Partial Molar Quantities

Equation (8.18) as applied to infinitely dilute solutions becomes

$$\frac{\partial \bar{Y}_1'/\partial x_2}{\partial \bar{Y}_2/\partial x_2} = 0 \qquad (8.47)$$

Two solutions of this equation exist [A40]; they are illustrated in Fig. 78*a* and *b*. The partial molar quantities (see Fig. 78*a*) for which

$$\lim_{x_2 \to 0} \frac{\partial \bar{Y}_1}{\partial x_2} = 0 \quad \text{and} \quad \lim_{x_2 \to 0} \frac{\partial \bar{Y}_2}{\partial x_2} \neq 0$$

include the partial molar volumes, enthalpies and heat capacities **(partial molar quantities of the first kind).** They are constant for the solvent and equal the molar quantities, i.e. $\lim_{x_2 \to 0} \bar{V}_1 = V_1^\circ$, $\lim_{x_2 \to 0} \bar{H}_1 = H_1^\circ$ and $\lim_{x_2 \to 0} (\bar{C}_p)_1 = (C_p^\circ)_1$ [see, for example, in Fig. 71 (p. 259) the values of $(\bar{C}_p)_{H_2O}$ at $x_{H_2SO_4} \to 0$ and $(\bar{C}_p)_{H_2SO_4}$ at $x_{H_2SO_4} \to 0$].

Thus, infinitely dilute solutions are characterized by the fact that the addition of the solvent is not attended by a change in volume, enthalpy and heat capacity of the system as a whole, i.e.

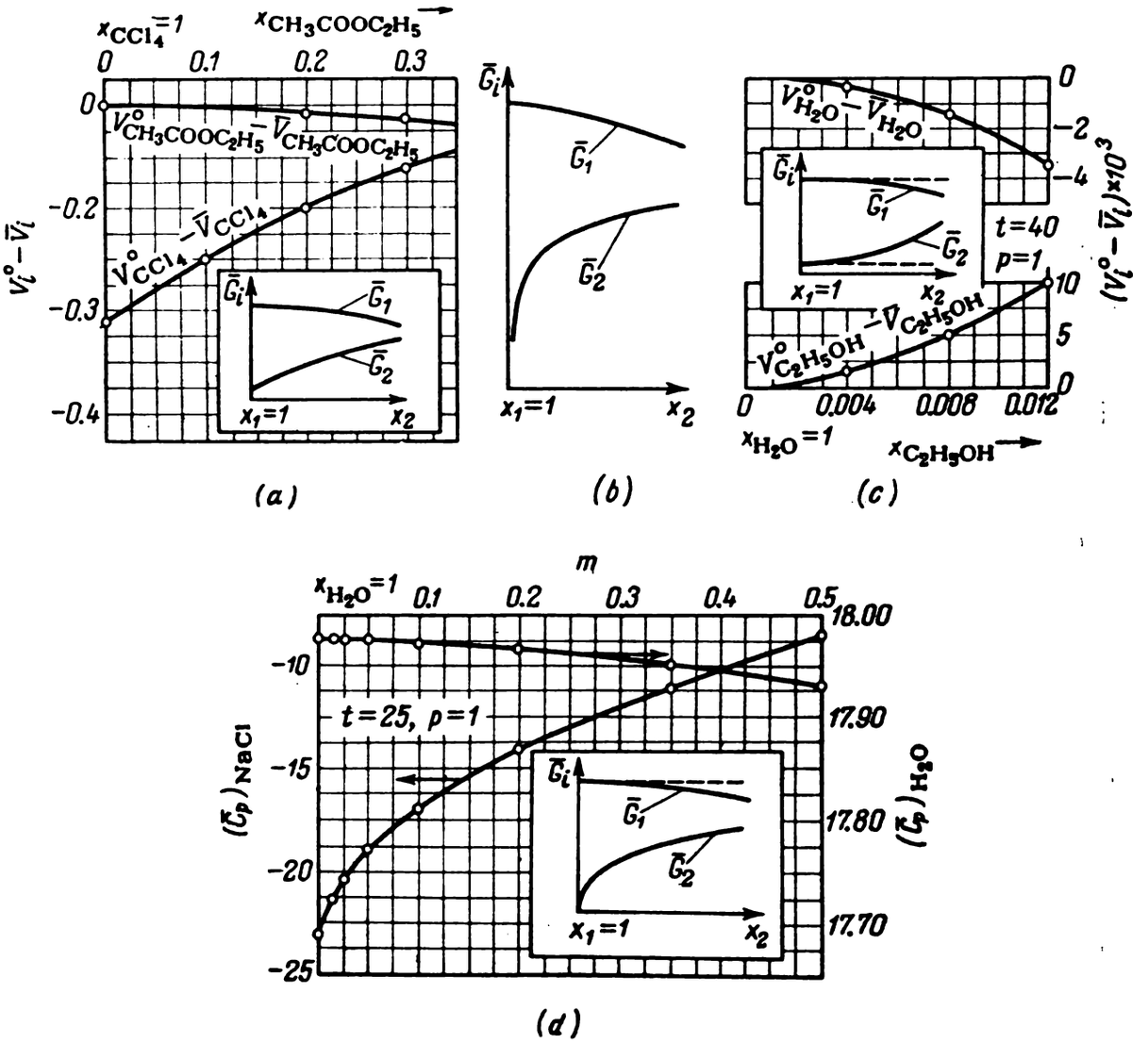

Fig. 78. Dependence of partial molar quantities on the concentration in an infinitely dilute solution :

$$a - \lim_{x_2 \to 0} \left(\frac{\partial \overline{Y}_1}{\partial x_2}\right)_{p,T} = 0, \quad \lim_{x_2 \to 0} \left(\frac{\partial \overline{Y}_2}{\partial x_2}\right)_{p,T} \neq 0;$$

$$b - \lim_{x_2 \to 0} \left(\frac{\partial \overline{Y}_1}{\partial x_2}\right)_{p,T} \neq 0, \quad \lim_{x_2 \to 0} \left(\frac{\partial \overline{Y}_2}{\partial x_2}\right)_{p,T} = \infty;$$

$$c - \lim_{x_2 \to 0} \left(\frac{\partial \overline{Y}_1}{\partial x_2}\right)_{p,T} = 0, \quad \lim_{x_2 \to 0} \left(\frac{\partial \overline{Y}_2}{\partial x_2}\right)_{p,T} = 0;$$

$$d - \lim_{x_2 \to 0} \left(\frac{\partial \overline{Y}_1}{\partial x_2}\right)_{p,T} = 0, \quad \lim_{x_2 \to 0} \left(\frac{\partial \overline{Y}_2}{\partial x_2}\right)_{p,T} = \infty$$

such solutions with respect to the solvent are ideal. The additivity of these properties is observed for infinitely dilute solutions in any state of aggregation and, in particular, for gas mixtures. This underlies the explanation of the fact that the fugacity rule (see

p. 275) is quite satisfactory for components in a great surplus even for pressures of several hundred atmospheres; it is quite accurate for the substance whose mole fraction is close to unity.

Figure 78*b* shows the influence of the concentration on the partial molar entropies and Gibbs energies **(partial molar quantities of the second kind)**; for them we have

$$\lim_{x_2 \to 0} \frac{\partial \overline{Y}_1}{\partial x_2} \neq 0 \quad \text{and} \quad \lim_{x_2 \to 0} \frac{\partial \overline{Y}_2}{\partial x_2} = \infty$$

i.e. the quantities $\overline{S}_i$ and $\overline{G}_i$ change with the concentration when $x_2 \to 0$.

Cases are known when $\overline{V}_1$ is also constant in the region of finite concentrations. It therefore follows from Eq. (8.17) that $\overline{V}_2$ is also constant in these cases. This conclusion, however, does not correspond to Fig. 78*a*. Mathematical analysis shows that the discrepancy obtained is imaginary. I. Krichevsky and Ya. Kazarnovsky [B60] found that three more cases complying with Eq. (8.47) are possible.

Indeed, Eq. (8.47) also holds when at $\partial \overline{Y}_2/\partial x_2 = 0$ the quantity $\partial \overline{Y}_1/\partial x_2$ with $x_2 \to 0$ tends to zero as a higher (than the first) power of x_2. Such a case is shown in Fig. 78*c*. It also corresponds to the partial molar enthalpies and heat capacities. Upon elevation of the temperature, when the anomalies in the properties of solutions diminish and the latter approach ideal ones, the possibility is not excluded of a transition from the case shown in Fig. 78*c* to constancy of the partial molar quantities of the first kind at finite concentrations. Therefore, in accordance with the extension of the region of concentrations in which a solution is ideal, the lines $\overline{Y}_1 = \varphi(x_2)$ and $\overline{Y}_2 = \varphi(x_2)$ will also be parallel to the axis of abscissas at finite values of x_2.

Still another case complying with Eq. (8.47) is possible when the numerator of the equation tends to zero as x_2^a, where $a < 1$. Here at $x_2 \to 0$, the denominator becomes equal to infinity (Fig. 78*d*). This case has been confirmed by experimental data in the system water-strong electrolyte.

As regards the case when

$$\lim_{x_2 \to 0} \frac{\partial \overline{Y}_1}{\partial x_2} = \infty \quad \text{and} \quad \lim_{x_2 \to 0} \frac{\partial \overline{Y}_2}{\partial x_2} = \infty$$

it apparently has no practical significance.

8.5.2. Henry's Law

The fugacity of the solvent in an infinitely dilute solution, as follows from the above, does not depend on the nature of the solute and is calculated by Raoult's law, i.e.

$$\lim_{x_2 \to 0} \frac{f_1}{x_1} = f_1^\circ = \varphi(p, T) \tag{8.48}$$

Since the fugacity of a liquid or of a solid solution equals that of the saturated vapour when the solvent in the gaseous state behaves like an ideal gas, Eq. (8.48) becomes

$$\lim_{x_2 \to 0} \frac{p_1}{x_1} = p_1^\circ = \varphi(T) \tag{8.49}$$

which coincides with Eq. (8.45).

Knowing the dependence of f_1 on the composition, we can easily find the dependence of f_2 on x_2. Using Eqs. (8.48) and (8.43), in accordance with Eq. (8.17) we get

$$x_1 \, dRT \ln (f_1^\circ x_1) + x_2 \, dRT \ln f_2 = 0$$

or

$$d \ln f_2 = -\frac{dx_1}{x_2} = \frac{dx_2}{x_2}$$

whence

$$\ln f_2 = \ln x_2 + \text{const}$$

Rewriting this equation in the form

$$\ln f_2 = \ln x_2 + \ln k(p, T)$$

we get for p, T = const

$$f_2 = kx_2 \quad \text{or} \quad \lim_{x_2 \to 0} \frac{f_2}{x_2} = k = \varphi(p, T) \tag{8.50}$$

If we consider f_2 in Eq. (8.50) as the fugacity of the solute in the gaseous phase coexisting with the liquid (solid) phase, it is the exact thermodynamic form of **Henry's law.** Its conventional wording — *the solubility of a gas is proportional to the pressure* (1802) — corresponds to the equation

$$\lim_{x_2 \to 0} \frac{p_2}{x_2^{lq}} = k \text{ or } x_2^{lq} = \frac{p_2}{k} \tag{8.51}$$

where p_2 = partial pressure of the dissolved gas
k = Henry's coefficient.

This equation holds within a certain interval of concentrations for any solution of a non-electrolyte if at $x_2^{lq} \to 0$ the fugacity of the solute coincides with its partial pressure. This is observed for a low (more precisely, an infinitely low) saturated vapour pressure and if the gaseous phase is a mixture of ideal gases.*

Thus, for an infinitely dilute solution, the fugacity of the solvent is calculated by Raoult's law, and that of the solute by Henry's law. Both laws hold for any state of aggregation of a solution.

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* For solvents with a high saturated vapour pressure, the substitution of the partial pressure for the fugacity even at $x_2^{lq} \to 0$ is not always permissible (see the following).

Although these laws establish the proportionality between the fugacity of a component of an infinitely dilute solution and its concentration, in the first of them the proportionality factor is the fugacity of the pure solvent, whereas in the second it does not have the physical meaning of the fugacity of the pure solute, because Henry's law, strictly speaking, is true for an infinitely dilute solution; it may never be extrapolated to a finite concentration. This is illustrated by Fig. 79 (where owing to the small value of the pressure, f_i is assumed to equal p_i): whereas in the region $x_1 \to 1$, the relationship $p_1 = \varphi(x_1)$ is expressed by a straight line coinciding with the line $p_1 = p_1^\circ x_1$, the relationship $p_2 = \varphi(x_2)$ is also linear, but deviates from the line $p_2 = p_2^\circ x_2$. The reverse relationship is observed in the region $x_1 \to 0$. This will be observed regardless of the nature of the vapour pressure curves, i.e. regardless of whether they are above the straight lines for an ideal solution (positive deviations) or under them (negative deviations) (see Chap. 10).

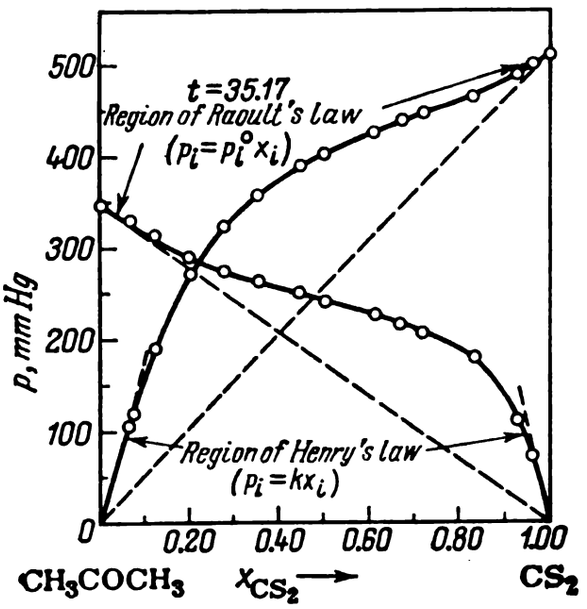

Fig. 79. Isotherms of vapour pressure in the system acetone-carbon disulphide. Checking of Eqs. (8.49) and (8.51)

With extension of the interval of concentrations corresponding to the ideal state of a solution, the straight portions of the curves grow in length. If a solution is ideal at all concentrations, then Eqs. (8.48) and (8.50), and for low pressures correspondingly Eqs. (8.49) and (8.51) become identical, i.e. Henry's coefficient acquires the meaning of the *fugacity* (pressure) *of the pure solute* at a pressure equal to the total pressure over the solution. In this case, the curves in figures like Fig. 78 become straight lines along their entire length (see Fig. 96, p. 320).

Example 11. What is the relationship between the volume of a gas dissolved in a liquid and the pressure at T = const?

Solution. If Eq. (8.51) holds for the process of solution, the weight amount of the dissolved gas increases in proportion to the pressure, but according to Eq. (6.5) the volume of a unit of its mass diminishes to the same extent. Therefore, the volume of the dissolved gas does not depend on the pressure. This is true only for low pressures, when the dissolving gas may be considered ideal.

Example 12. Find an equation for calculating the osmotic pressure. What will be the form of this equation if a solution has the properties (a) of an ideal solution, and (b) of an infinitely dilute solution?

Solution. Assume that the solution is separated from the solvent by a semipermeable membrane through which only molecules of the solvent can pass, and which is impermeable to molecules of the solute (Fig. 80). Since x_1 in the solution is less than unity, the fugacity of the pure solvent is greater than its fugacity in the solution, i.e. $G_1 > \bar{G}_1$. Therefore, when the pressure on both pistons is the same at a given temperature, the solvent will pass into the solution. If this process were not attended by the creation of a difference of levels, it would have continued up to a levelling out of the concentrations, i.e. to infinite dilution of the solution. The value of $\bar{G}_1$ can be raised to G_1 artificially by isothermally increasing the pressure on the right-hand piston from p° to p. The quantity $p - p^\circ = \Pi$ is the **osmotic pressure.** In other words, when the pressure grows to a value at which the fugacity of the solvent will be the same at both sides of the membrane, the equilibrium violated by solution will be restored.

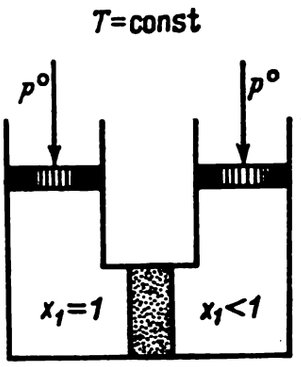

Fig. 80. Semipermeable membrane and osmotic pressure. To Example 12

From Eq. (8.7) we get

$$G_1^\circ - \bar{G}_1 = \int_{p^\circ}^{p} \bar{V}_1 \, dp$$

(a) For an ideal solution, according to Eqs. (8.38) and (8.42), this equation becomes

$$-RT \ln x_1 = V_1^\circ (p - p^\circ) = V_1^\circ \Pi$$

(we disregard the dependence of V_1° on p).

(b) Expanding $\ln x_1 = \ln (1 - x_2)$ into a series * and discarding the higher terms of the expansion (because in an infinitely dilute solution $x_2 \to 0$), we get the equation

$$\Pi = \frac{x_2 RT}{V_1^\circ} = cRT$$

coinciding with the Mendeleev-Clapeyron equation. Therefore, *the osmotic pressure equals the pressure which would be exerted by the solute if in the form of an ideal gas it occupied the same volume at the same temperature.* This is the **van't Hoff law** (1887). It is clear that the formal applicability of an equation of state of an ideal gas does not mean similarity between the gaseous and dissolved states.

* $\ln (1 - y) = -y - \frac{y^2}{2!} - \frac{y^3}{3!} - \ldots$

Chapter 9

BINARY SOLUTION-PURE COMPONENT EQUILIBRIUM

Systems differing in the state of aggregation of either the solution or the pure component may be encountered among "binary solution-pure component" systems, but all of them have similar properties and can be described by common equations. This chapter treats only a few of these systems. Systems in which a liquid solution is in equilibrium with a pure solid or gaseous substance, and also systems consisting of a gaseous solution and a liquid are the most important for practical purposes. This chapter examines the relationship between the temperature and concentration and between the pressure and concentration of a solution. In each case, one of the parameters is fixed (in the first — the pressure, in the second — the temperature), and therefore the phase rule is applied, unless otherwise indicated, in the form of Eq. (5.49), i.e. the conditional variance is determined; the actual variance will be greater by one.

The method of **physicochemical analysis** developed by N. Kurnakov and based on a study of "property-composition" diagrams for various systems is widely used in this and the next two chapters.

One of the phases in all these systems is a pure substance, which permits us to do without the superscripts for purposes of simplification. Since either the first or the second component may be in equilibrium with the solution, only the subscript "i" is used to denote the properties of a pure component in deriving the general relationships.

9.1. RELATIONSHIP BETWEEN TEMPERATURE AND CONCENTRATION

The introduction of another substance into a "solid component-liquid component" equilibrium system violates equilibrium, and at a constant pressure the temperature of the system changes so as to restore it, i.e. prevent solution.

In accordance with Eq. (5.49) at p = const, the given system will be conditionally univariant, i.e. $x_i = \varphi(T)$, where x_i is the concentration of a solution saturated with the i-th component. If the temperature is isobarically changed by dT, a change in the concentration of the solution by dx_i will cause equilibrium to set in again. This means that $dG_i = d\bar{G}_i$, i.e.

$$\left(\frac{\partial G_i}{\partial T}\right)_p dT = \left(\frac{\partial \bar{G}_i}{\partial T}\right)_{p, x_i} dT + \left(\frac{\partial \bar{G}_i}{\partial x_i}\right)_{p, T} dx_i$$

or in connection with Eqs. (5.24) and (8.5)

$$-S_i\, dT = -\bar{S}_i dT + \left(\frac{\partial \bar{G}_i}{\partial x_i}\right)_{p, T} dx_i$$

The inequality of S_i and $\bar{S}_i$ is compensated by a change in the concentration.

This process is reversible because of the fact that both before and after the temperature change the system is in equilibrium, and its temperature and concentration in the initial state differ from these quantities in the final state by an infinitely small amount.

On the basis of Eq. (4.8), which here can be written down as

$$\bar{S}_i - S_i = \frac{\bar{H}_i - H_i}{T}$$

we finally obtain

$$\left(\frac{\partial x_i}{\partial T}\right)_{p, \text{eq}} = \frac{\bar{H}_i - H_i}{T(\partial \bar{G}_i/\partial x_i)_{p, T}} \tag{9.1}$$

where $\bar{H}_i - H_i$ is the differential heat of solution in a solution *saturated* with the i-th component (determined by extrapolation).

The quantity $\bar{H}_i - H_i$ may differ from the differential heat in unsaturated solutions not only in magnitude, but also in sign. Therefore care should be taken when determining the sign of $\partial x_i/\partial T$ on the basis of experimental data.* The solubility of a number of substances that dissolve in a *pure solvent* with the liberation of heat (certain salts in water are an example) is known to grow with increasing temperature. There is only a seeming contradiction here to the principle of displacement of equilibrium — its application is limited to saturated solutions (an equilibrium system!), and for a saturated solution the values of the heat of solution for these systems are positive.

* The quantity $\partial \bar{G}_i/\partial x_i$ is positive (see, for example, [A22]).

Equation (9.1), corresponding to the solution-pure component equilibrium curve (in the coordinate temperature-composition at p=const), is absolutely accurate but is almost never used directly, because the dependence of $\overline{G}_i$ on x_i is usually unknown.

Equation (9.1) can be found from Eq. (8.21). Indeed, in the given case (p = const, $x_i'' = 1$), Eq. (8.21) becomes

$$(\overline{S}_1 - S_1)\,dT + x_2 \frac{\partial^2 G}{\partial x_2^2} dx_2 = 0$$

$$(\overline{S}_2 - S_2)\,dT - x_1 \frac{\partial^2 G}{\partial x_2^2} dx_2 = 0$$

whence, keeping Eq. (8.20) and the reversibility of the process in mind, we get Eq. (9.1).

9.1.1. Solution-Solid Component Equilibrium

Since $\partial \overline{G}_i/\partial x_i > 0$, the sign of $\partial x_i/\partial T$ is determined by that of $\overline{H}_i - H_i$. By conditionally dividing it into the heat of fusion of the pure component and the differential heat of dilution

$$\overline{H}_i - H_i = [(H_i^{lq}) - (H_i^c)] + [\overline{H}_i - (H_i^{lq})]$$

we conclude that the differential heat of solution may be positive or negative: the first addend characterizing the transition of the solid component into the state of aggregation in which it is in the solution is positive; the second addend characterizing the interaction in the solution is negative. Therefore, if the value of the latter is great (for example when many substances forming crystallosolvates are dissolved), the heat of solution is negative, and in accordance with Eq. (9.1) the solubility will diminish with increasing temperature. In other words, the freezing point will lower with growing concentration.

Ideal Solution. Equation (9.1) for an ideal solution, in connection with Eq. (8.44), transforms into an equation called **Schröder's logarithmic curve** (1890)

$$\left(\frac{\partial \ln x_i}{\partial T}\right)_{p,\,eq} = \frac{H_i^\circ - H_i^c}{RT^2} \tag{9.2}$$

Although in an ideal solution $\overline{H}_i = H_i^\circ$ [Eq. (8.39)], this is not an indication that the solubility does not depend on the temperature (or the freezing point on the concentration), because the pure component and the solution are in *different* states of aggregation. The numerator of the right-hand side of Eq. (9.2) equals the heat of fusion (to a supercooled liquid). If the solute were liquid at the given temperature, its solubility in an ideal solution would not depend on the temperature. Consequently, the solubility in an ideal

solution will be limited only when $t < (t_m)_i$, i.e. when the pure component is in a different state of aggregation. Since $\Delta H_f > 0$, the solubility always grows with increasing temperature.

Integrating Eq. (9.2) — the left-hand side within the limits from 1 to x_i, and the right-hand side from $(T_m)_i$ to T — and assuming that ΔH_f is constant within the interval from $(T_m)_i$ to T, we get

$$\log (x_i)_T = \frac{(\Delta H_f)_i}{4.576}\left[\frac{1}{(T_m)_i} - \frac{1}{T}\right] = -\frac{(\Delta H_f)_i}{4.576}\frac{(T_m)_i - T}{(T_m)_i T} \qquad (9.3)$$

It is easy to verify this equation graphically (Fig. 81); if a solution is ideal, the relationship $\log x_i = \varphi(T^{-1})$ is linear; when continued to the region of high temperatures, the straight line will reach the point with the coordinates $\log x_i = 0$ and $T^{-1} = (T_m)_i^{-1}$ and will have a slope corresponding to the value of $(\Delta H_f)_i$. In these cases, Eq. (9.3) or its corresponding graph is convenient for finding the solubility (or freezing point) by extrapolation.

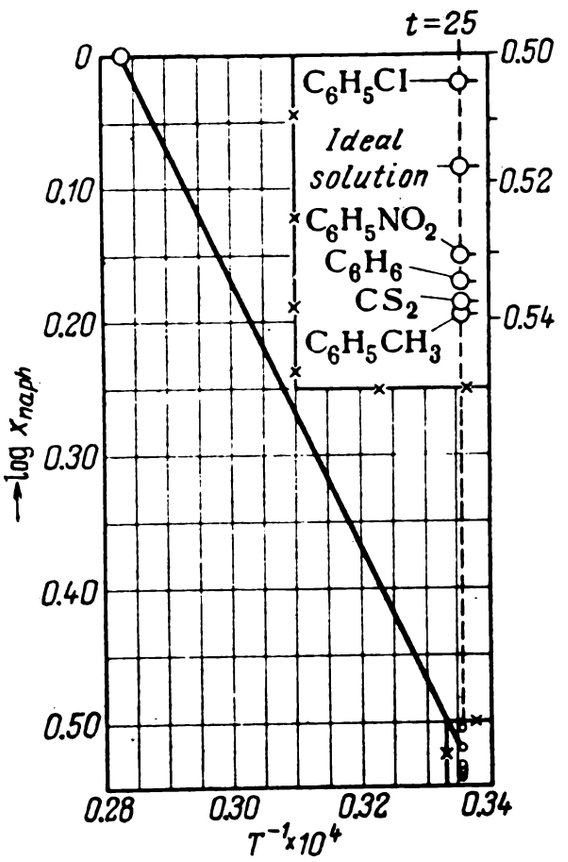

Fig. 81. Temperature dependence of solubility of naphthalene in selected solvents.

Checking of Eq. (9.3). (See Example 1)

Since ΔH_f changes insignificantly with temperature, and the possible difference of temperatures is not great, then by assuming that $\Delta H_f = \text{const}$, we get sufficiently satisfactory results. For greater accuracy, we must take into account the influence of T on ΔH_f (see Sec. 7.4). In the first approximation, it may be assumed that the difference between the heat capacities of substances in the solid and liquid states is constant.

It follows from Eq. (9.3) that the solubility (or change in the freezing point) of a given substance in all the solvents with which it forms an ideal solution does not depend on the nature of the solvent, but depends only on the value of the temperature (concentration) (see Fig. 81). It is also apparent from this equation that a substance with a high melting point has a lower solubility than a low-melting substance; the latter conclusion is the more correct, the closer are the heats of fusion of the substances being compared.

If we consider a solution within the interval from $x_1 = 1$ to $x_2 = 1$, we should bear in mind that at one set of concentrations it is saturated with the first component, and at another with the second component. To construct solution-pure component equilibrium curves for both substances (a **melting diagram,** Fig. 82), Eq. (9.3) should be used for each substance:

$$\left.\begin{aligned}\log (x_1)_T &= \frac{(\Delta H_f)_1}{4.576}\left[\frac{1}{(T_m)_1} - \frac{1}{T}\right] \\ \log (x_2)_T &= \frac{(\Delta H_f)_2}{4.576}\left[\frac{1}{(T_m)_2} - \frac{1}{T}\right]\end{aligned}\right\} \quad (9.4)$$

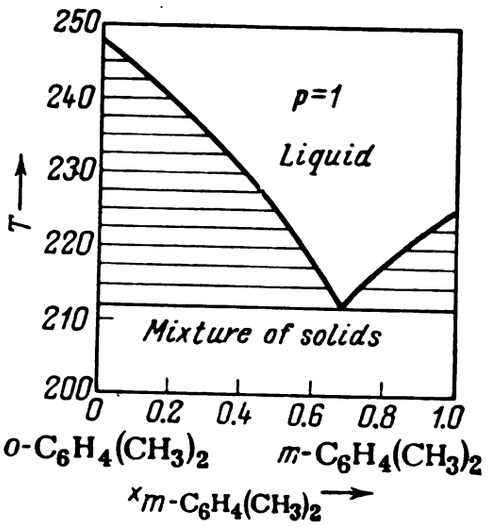

Fig. 82. Melting (phase) diagram for non-isomorphic systems with a simple eutectic.
System *o*-xylene-*m*-xylene.
The freezing curves were plotted by Eq. (9.4)

The freezing (melting) curves intersect at the **eutectic point,** which corresponds to simultaneous saturation of a solution with both components. Its coordinates are determined by simultaneously solving Eqs. (9.4) or by graphical extrapolation.

Inspection of Fig. 82 shows the conditional nature of opposing a solvent to a solute on the basis of the features indicated on p. 251.

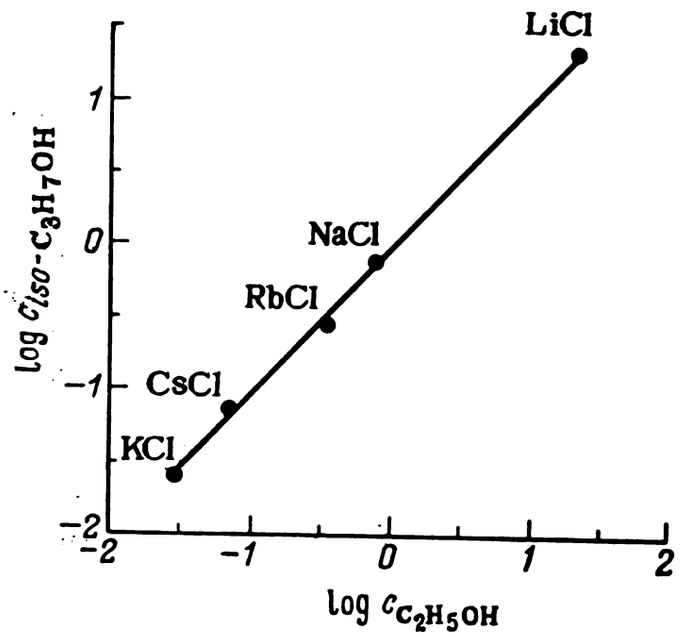

Fig. 83. Relationship between solubility of alkali metal chlorides in ethanol and isopropanol at 25 °C

The freezing curves will not be exactly logarithmic for non-ideal solutions, but their nature will not change, i.e. their concavity will face the axis of abscissas. Systems are known, however, where despite Eq. (9.2), according to which $(\partial^2 T/\partial x_i^2)_{p,\,eq} < 0$, the convexity of the freezing curves faces the axis of abscissas.

The deviation from Eq. (9.2) will be about the same for solutions of similar substances, hence in the first approximation the relationship shown in Fig. 83 for one example will hold for them. This relationship is similar to Eq. (7.8) and is

a special case of the first method of comparative calculations [B45]. Figure 84 shows an example of inversion of the fourth method [see the analogue — Eq. (7.7)].

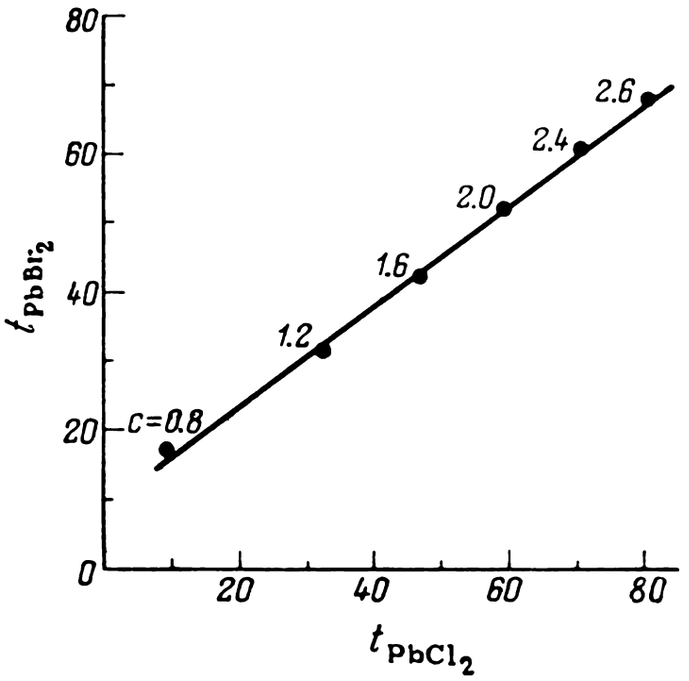

Fig. 84. Relationship between temperatures of saturated solutions of $PbCl_2$ and $PbBr_2$ at equal concentrations

Example 1. Find the solubility of naphthalene ($C_{10}H_8$) at t_m = = 80 °C in nitrobenzene ($C_6H_5NO_2$) at 50 °C and the heat of solution of naphthalene if its solubility at 25 °C is $x_{naph} = 0.295$. Consider the solution of naphthalene in nitrobenzene to be ideal.

Solution. We use two points [$x_{naph} = 1$, $T = (T_m)_{naph} = 353.2$ K and $x_{naph} = 0.295$, $T = 298.2$ K] to plot a graph in the coordinates $\log x_{naph} = \varphi(T^{-1})$ (see Fig. 81), and by interpolation find $x_{naph} =$ = 0.54. The heat of solution of naphthalene according to Eq. (9.3) is determined from the slope of the straight line; it equals 4650 cal/mol, which differs from the heat of fusion of naphthalene (4560 cal/mol [D4], 7: 325) by 2%. It is precisely this quantity that determines the degree of deviation of the given solution from an ideal one, which can also be seen in Fig. 81. The top right-hand corner of this figure shows to an enlarged scale the solubility of naphthalene in various solvents, including nitrobenzene, at 25 °C.

Infinitely Dilute Solutions. The relationship between the temperature and concentration for a poorly soluble (more exactly for an infinitely poorly soluble) substance is expressed by Eq. (9.2), since with respect to the solvent, an infinitely dilute solution is ideal (see Sec. 8.5.1).

Let us write down Eq. (9.2) for the solvent, using $\ln (1 - x_2)$ instead of $\ln x_1$. By expanding this expression into a series, discarding the higher terms of the expansion and considering that when $x_2 \to 0$ we have $T(T_m)_1 \approx (T_m)_1^2$, we get

$$\left(\frac{\partial T}{\partial x_2}\right)_{p, eq} = -\frac{R(T_m)_1^2}{(\Delta H_f)_1} \tag{9.5}$$

To apply Eq. (9.5) for solutions in which the concentration of the first component is infinitely small, it is sufficient to change the places of the subscripts 1 and 2.

Equation (9.5) shows that there is a *linear* relationship between the concentration and the temperature in an infinitely dilute solution. This means that in a melting diagram for *any* system (in which no solid solutions form) the ends of the freezing curves for each component are *always* straight over a certain length. It is easy to find the heat of fusion of the relevant component by Eq. (9.5) according to the slope of these straight lengths.

The depression (because the right-hand side of the equation is negative) of the freezing point of a solution is proportional to the concentration, and the proportionality factor (the **cryoscopic** * **constant** or the **freezing-point lowering constant**) does not depend on the nature of the solute. Thus, if water is the first component, then substituting in Eq. (9.5) the molality for the mole fraction and the quantity $d[(T_m)_{H_2O} - T] = d\theta$ (where θ is the depression of the freezing point) for dT, we shall find the cryoscopic constant of water

$$\left(\frac{\partial \theta}{\partial m}\right)_{p, eq} = \frac{R(T_m)_{H_2O}^2}{55.51\ (\Delta H_f)_{H_2O}} = \frac{1.987 \times 273.2^2}{55.51 \times 1438} = 1.858$$

The following must be borne in mind:

1. Equation (9.5) and its corollaries cannot be applied to solutions of electrolytes.

2. The cryoscopic constants do not equal the observed depression of the freezing point of a solution at a concentration of unity, but are *extrapolation* constants, i.e. equal the depression of the freezing point of an infinitely dilute solution reduced to a concentration of unity (Fig. 85).

3. If both components are in the solid phase, i.e. a solid solution is formed, its freezing point may not only be lower than the freezing point of the solvent, but also be equal to and even greater than it.

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* From the Greek "kryos" — frost, ice and "skopein" — to look.

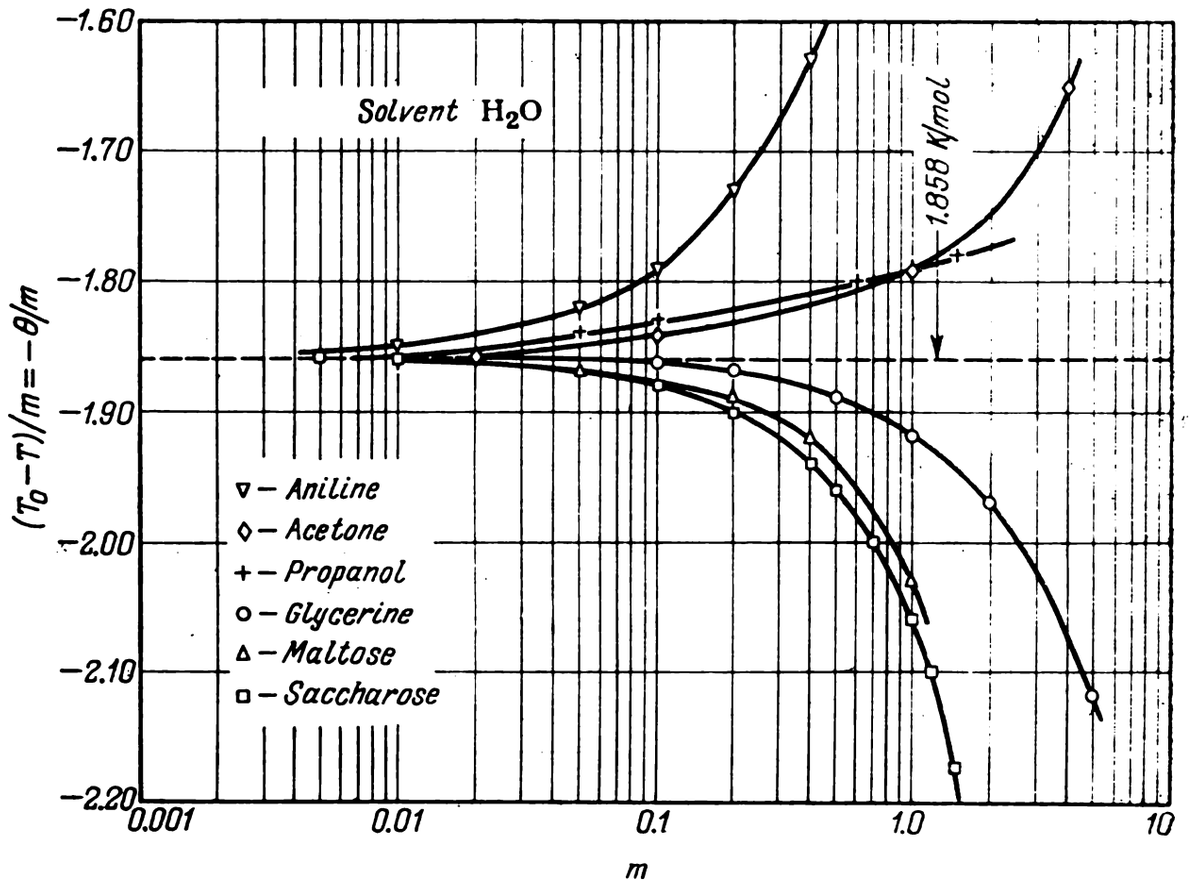

Fig. 85. Dependence of freezing point on concentration of solution. Checking of Eq. (9.5)

9.1.2. Analysis of Solubility Diagrams

Non-Isomorphic Mixtures Forming No Chemical Compounds. The concentration of a solution, temperature and pressure can be variables in the general case. A three-dimensional diagram is therefore needed such as that shown in Fig. 86. Surfaces *a'aa''e''ee'* and *e'ee''b''bb'* are fields of freezing of the first and second substances. Since ΔH_f and T_m change appreciably only upon a very great change in pressure, the temperature dependence of the solubility for various pressures is about the same (the influence of the pressure is shown conditionally in Fig. 86). Hence curves *a'aa''* and *b'bb''* are close to horizontal lines. If we took water or bismuth as one of the substances, the freezing curve would have a negative slope (because $\Delta V_m < 0$ for them, see p. 208).

Consider an isobaric section of the diagram, i.e. plane *AaebB* (see also Fig. 82). At any point above freezing curves *ae* and *be* between the vertical lines of the pure components, the system is single-phase (liquid), and therefore is conditionally * (p = const) bivariant. This means that within *definite limits*, without violating

* The word "conditionally" is omitted in the following.

the nature of a system, we can vary the temperature and composition *independently of each other*. On curves *ae* and *be* (except for point *e*) the system is also bivariant (only the interval of variation of *t*

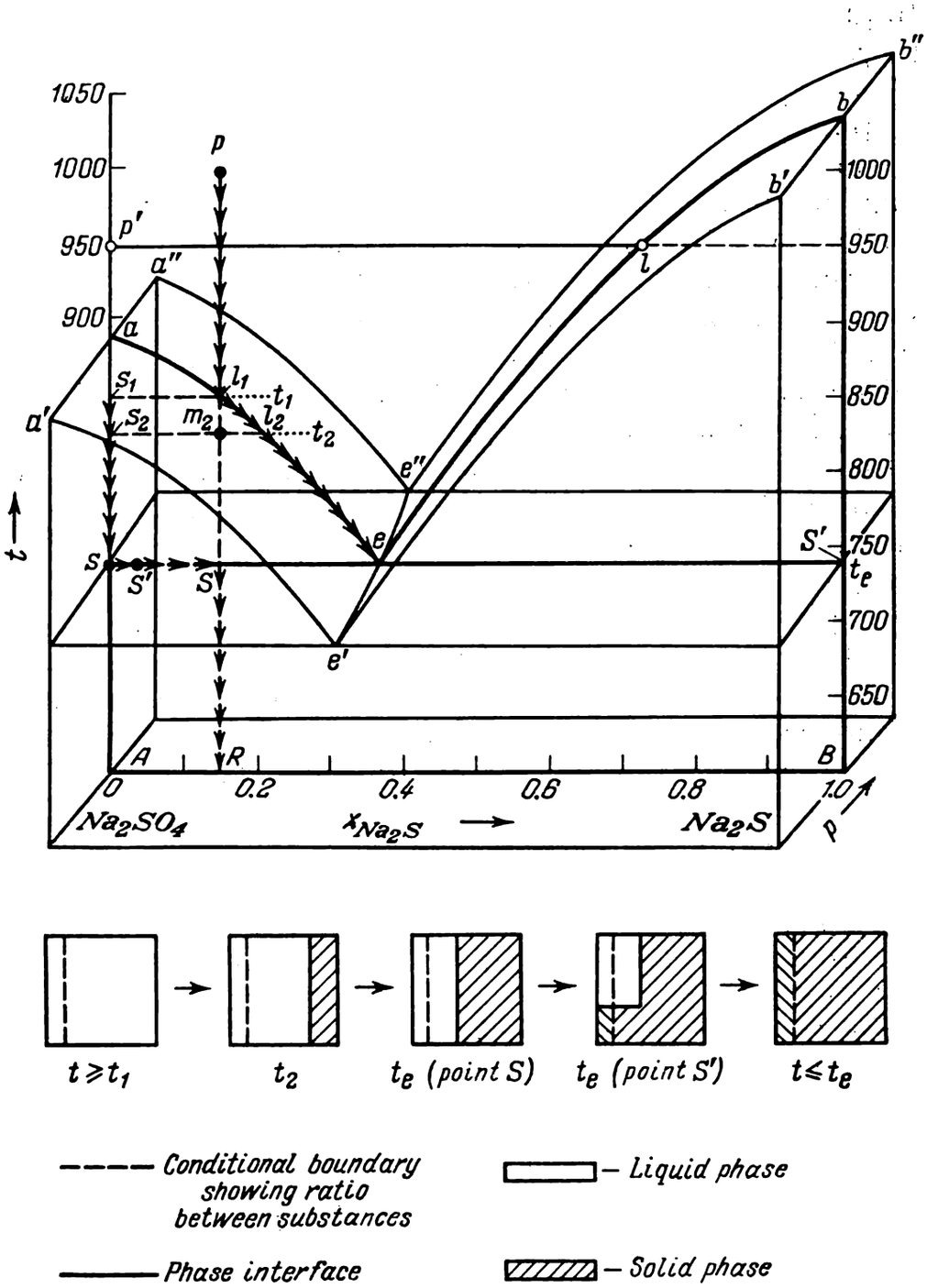

Fig. 86. Relationship *x-t-p* for two-component non-isomorphic mixtures.
System Na_2SO_4-Na_2S. (See Example 2)

and x_i is limited). Above and below points *a* and *b* of freezing (melting) of the pure substances, it is univariant. For points *a* and *b*, two cases can be conceived: at the moment of "reaching" them or "emerging" from them the system is also univariant; at interme-

diate moments a liquid and a solid phase coexist, and the system becomes invariant. Matters are similar at eutectic * point e: when the system "reaches" it (along a vertical line), it is single-phase (liquid), and when it "emerges" from it, the system is two-phase (crystals of A and B coexist); only at intermediate moments do all three phases coexist, i.e. the system becomes invariant.

The application of the phase rule in other regions of the diagram will be considered in connection with an analysis of the process of cooling of an unsaturated solution having the composition P. When cooled to t_1, the system will be liquid. At point l_1, the solution will be saturated with substance A. The removal of the heat δQ will cause an infinitely tiny crystal of this substance to appear (theoretically at $t_1 - dt$; the corresponding point on vertical line $P'A$ will be slightly below point s_1). As A freezes out, the solution becomes enriched with component B and the freezing point lowers, i.e. the figurative point slides downward along curve ae. The figurative point of the solid phase moves along straight line as. When t_e is reached, the solution also becomes saturated with substance B. Hence, beginning from this moment, the remaining liquid will freeze completely without changing its composition. The freezing of both substances (a **eutectic mixture,** and in the case of a solution of a salt in water a **cryohydrate**) leads to a change in the composition of the solid part of the system, because the content of substance B in it grows (and the content of A diminishes). This change is shown by straight line sS.

If we fix the composition of the system at the moment corresponding to point S', we shall find that about 35% of the liquid solution (or about 80% of the total mass) of composition e has frozen. After the last drop of liquid disappears, the composition of the frozen mass will correspond to point S on the same vertical line as point P; the temperature will again begin to lower (line SR) until the removal of heat is stopped.

If we take a solution of any other composition, then the freezing of non-eutectic solutions (non-cryohydrate brines) begins with the substance whose amount is greater in comparison with the eutectic (cryohydrate). In freezing, the initially formed crystals grow, and then the eutectic mixture which begins to freeze out at t_e fills the space between them in the form of fine crystals. The latter circumstance is explained by the fact that crystals of different substances owing to the approximately identical rate of freezing prevent one another from growing to considerable dimensions. An exception is a eutectic solution, for which complete freezing is observed at point e with the formation of a eutectic mixture.

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* From the Greek "eutectic" — well-melting.

Within the interval from t_1 to t_e, the system is univariant, i.e. either the temperature or the concentration can be changed arbitrarily. If, for instance, at a given pressure we fix the temperature, then we thus also determine the concentration of a saturated solution (which, for example, can be found by Schröder's logarithmic curve for an ideal solution). This conclusion holds with respect to any systems whose figurative points are below curves *ae* and *be*. It must be borne in mind that any point corresponding to heterogeneous systems (for example point m_2) is deprived of a physical meaning (a *single* point cannot characterize *two* phases differing in composition), i.e. is not a phase point, but a point of a system. A three-phase system characterized by point *e* is invariant — at a given pressure neither the temperature nor the concentration can be changed.

If the eutectic (cryohydrate) were a chemical compound, then there would be four phases at point *e* (a liquid and a solid pure substances, and a chemical compound), and $f = 2 - 4 + 1 = -1$. A eutectic mixture is not a compound, which can also be confirmed by the following: a change in pressure causes not only its melting point, but also its composition, to change. The nature of the change in the melting point of a eutectic with pressure is determined by the sign of ΔV_m. Hence, the melting point of a cryohydrate drops with a growth in pressure. The change in the composition of a eutectic mixture is determined by the relationship between the quantities $(\partial T_m/\partial p)_1$ and $(\partial T_m/\partial p)_2$ — it becomes richer in the component for which this derivative is lower. Since ΔV_m is very small, however, the change in composition with a change in pressure is great only with a considerable change in the pressure; for example a eutectic mixture consisting at $p = 1$ atm of 88% of Al and 12% of Si contains 18% of Si at $p = 18\,000$ atm.

Below t_e (line SR) the system again becomes univariant, since the liquid phase disappears. All the systems characterized by points in region $Ass'B$ of the diagram are univariant. They consist of pure solids.

The application of the lever rule to this process at the cooling stages discussed is shown in the bottom part of Fig. 86.

In practice, a solution may also be supercooled; in this case solutions characterized by points below curves *ae* and *be* (for example by point m_2) are said to be supersaturated. But as a result of shaking or introducing a seed, partial freezing occurs, and the figurative point "floats up" to the freezing surface. Here freezing occurs at a temperature below the beginning of equilibrium freezing: as the temperature rises, a certain amount of crystals of the first substance will be formed, causing the composition of the liquid phase to change in comparison with the initial one, i.e. the figurative

point will be to the right and below point l_1. Greater supercooling will be attended by a bigger change in the composition of the liquid phase and a greater displacement of the figurative point. In freezing from a mixture richer in the second substance than the eutectic mixture, the point in the given process will be to the left of the initial one. Consequently, in both cases to properly determine the freezing point, it is necessary to slowly heat a supercooled mixture in which crystallization has occurred and watch the temperature at the moment the last crystal disappears.

If a solid solution were heated, the above phenomena would proceed in the reverse direction. For instance, by heating a mixture of ice and a salt having the composition R (Fig. 87), at t_e we get the first drop of the liquid phase having the composition e (point S). The system will become invariant, and elevation of the temperature will stop, i.e. the heat supplied will be used for melting.* Point e is to the left of S, therefore more ice than salt will melt out of the mixture, and the solid mixture will become relatively enriched with salt. After the last crystal of ice vanishes, the system will become univariant, the temperature will begin to rise and the composition of the solution will change, because only the remaining salt passes into it. The composition of the liquid phase (saturated solution)

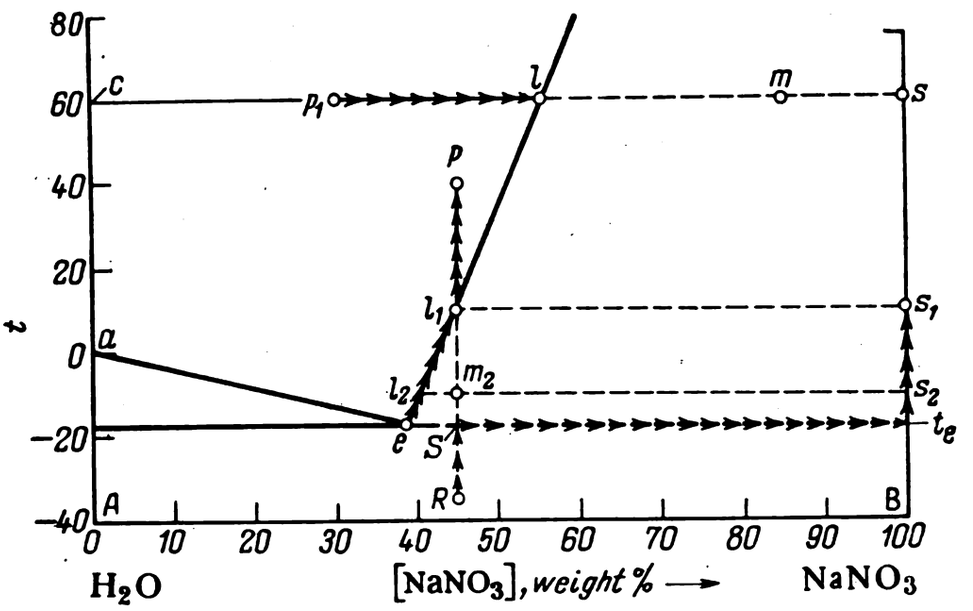

Fig. 87. Phase diagram with a single eutectic.
System H_2O-$NaNO_3$

corresponds to curve el_1. If the heating process is stopped at a temperature corresponding to point m_2, then the fraction of the solid

* The eutectic mixture has the lowest melting point; therefore the composition of the first drop does not depend on that of the initial mixture.

salt will equal l_2m_2/l_2s_2. At a temperature corresponding to line l_1s_1, the last crystal of the salt will disappear (point s_1), and the entire system will become homogeneous, transforming into a saturated solution of composition l_1 (the arm of the solid phase now equals zero). With vanishing of the solid phase, the system becomes bivariant.

The process of **isothermal evaporation** is also of practical interest for salt solutions. We shall evaporate a brine characterized by point P_1. At a concentration corresponding to point l, it will become saturated, and after the removal of the heat δQ a small crystal of the salt appears (point s). Since according to the phase rule, the concentration of a saturated solution at a given pressure is determined only by the temperature, further evaporation will not cause a change in the composition of the solution, i.e. in the position of point l. Along $P_1 - l$, the points of the system coincide with the phase points; beginning from point l, they travel along straight line ls, whereas the phase points (l and s) remain where they were. The proportions between the amounts of the phases are determined according to the lever rule (proved on p. 322). Thus, in the system whose total composition is shown by point m, the amount of the solid phase will be about twice that of the liquid one, and the amount of evaporated water can be determined from the proportion

$$\frac{\text{amount of evaporated water}}{\text{amount of solution and solid salt}} = \frac{P_1m}{cP_1}$$

For other systems, we shall also limit ourselves to a discussion of the orthogonal projection of the three-dimensional diagram onto the temperature-composition coordinate plane, since the relationship between solubility and temperature (the freezing point and the composition of a solution) is the most important.

Example 2. Using the melting diagram for the system Na_2SO_4-Na_2S (see Fig. 86), find the amount of coal needed to reduce 100 kg of sodium sulphate according to the reaction $Na_2SO_4 + 2C = Na_2S + 2CO_2$ if it is conducted at $t = 950\,°C$ to the beginning of freezing of the solution.

Solution. Point P' corresponds to the conditions in which the reaction begins, and point l to the conditions in which it terminates. At the latter point, the system will consist of 28% of Na_2SO_4 and 72% of Na_2S.

We find the amount of reacted sulphate m from the relationship

$$\frac{78}{142}m/(100 - m) = \frac{72}{28}, \text{ whence } m \approx 82.5 \text{ kg}$$

Denoting the amount of coal needed by y, we get

$$\frac{Na_2SO_4}{2C} = \frac{142}{24} = \frac{82.5}{y}$$

whence $y \approx 14$ kg.

Non-Isomorphic Mixtures Forming Stable Chemical Compounds. When two substances form a stable chemical compound, the diagram has the form shown in the top left corner of Fig. 88. The diagram will have such a form particularly when A is H_2O and B is an anhydrous salt, i.e. D is a crystallohydrate. In this case, the eutectic point will be a cryohydrate one, point D corresponds to a crystallohydrate, and point P_2' to its melting point. If the compound is stable, the peak at P_2' will be sharp, whereas if it partly dissociates, the peak will be flat, because in the latter case the freezing point of D will be lowered owing to the presence of dissociation products (A and B) in the system.

If the mole fraction (mole per cent) is laid off along the axis of abscissas, then the position of point D permits us to judge directly the composition of the compound.

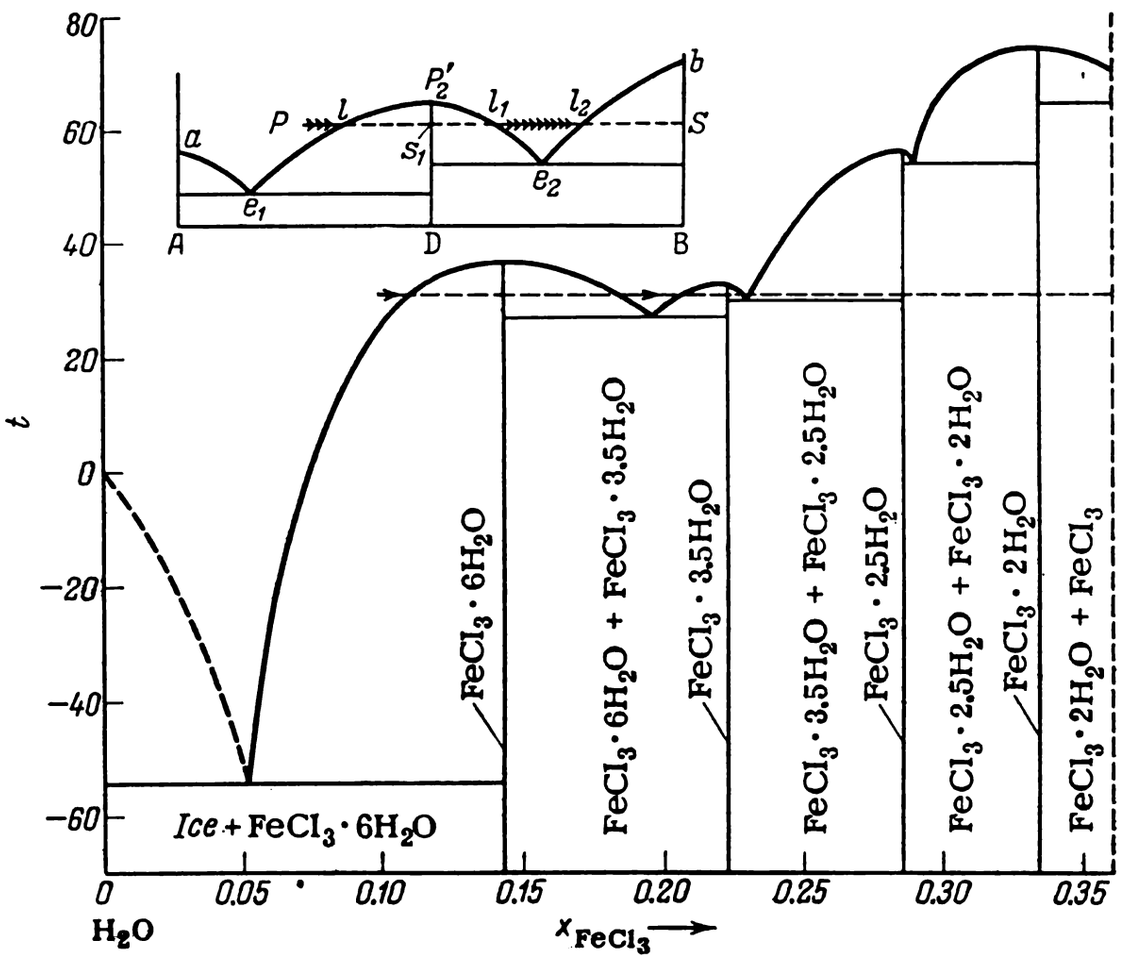

Fig. 88. Phase diagram for non-isomorphic systems forming a stable chemical compound.
System H_2O-$FeCl_3$

A diagram with one stable compound can be considered as formed of two simple diagrams (see Figs. 82 and 86). The corresponding substances freeze along curves ae_1 and be_2, and the compound along P'_2e_1 and P'_2e_2. Should A and B form several compounds, then the diagram becomes more complicated: several peaks appear whose number equals that of the compounds. For example, the diagram of the system H_2O-$FeCl_3$ in Fig. 88 has such a form.

Assume that component A is water and B is a salt, and consider the process of isothermal evaporation of water from a brine whose composition is characterized by point P (see Fig. 88). At point l, precipitation of the crystallohydrate begins (the composition and temperature of the solid phase are determined by point s_1). Upon further evaporation (displacement of the point of the system from l to s_1), the composition of the equilibrium phases will remain unchanged (since p, T=const), and only their ratio will change. When the composition of the system coincides with that of the compound (point s_1), the last droplet of the saturated brine having the composition l will vanish. Further dehydration leads to gradual evaporation of the water of crystallization with the formation of a saturated solution of the crystallohydrate having the composition l_1. The fraction of the liquid phase will grow, and at the moment when the composition of the system corresponds to point l_1, the entire phase will melt. The system will remain homogeneous until its composition takes on the value corresponding to point l_2. At this composition, the solution becomes saturated, and freezing of the anhydrous salt begins (at a constant composition of the solution). Its amount will grow as evaporation proceeds, and, finally, all the water will be removed (point S).

A similar, but somewhat more complicated process will occur when a weak (for example 10%) solution of $FeCl_3$ is evaporated at $t = 31\,^\circ C$. This process is shown in Fig. 88 by a straight dotted line. After the above description, it is simple to follow the reverse process of isothermal hydration of the salt (the transition from point S to point P in Fig. 88).

A chemical compound can be in equilibrium with two different liquid solutions (and a crystallohydrate with two different brines). If the temperature is below t_{e2}, then the process of isothermal evaporation of the brine, occurring up to precipitation of the crystallohydrate like the above process, will further change. After the formation of a crystallohydrate, evaporation of the water results in dehydration of the crystals without the appearance of a liquid phase.

In this case, the compound is stable at its melting point, the composition of the solid and liquid phases is identical, and therefore the compound is called **congruent***.

* From the Latin "congruentem" — corresponding.

Non-Isomorphic Mixtures Forming an Unstable Chemical Compound. If components form a compound (for instance a crystallohydrate) that decomposes below the melting point, the solubility

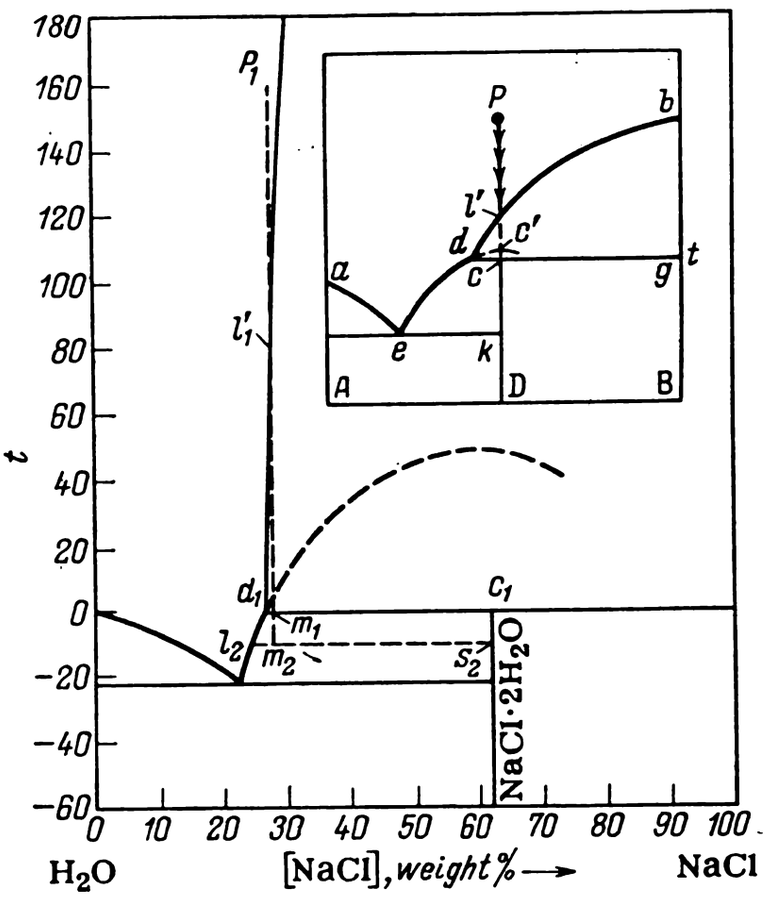

Fig. 89. Phase diagram for non-isomorphic systems forming an unstable chemical compound.
System NaCl-H_2O. (See Example 3)

curves have a hidden peak (see the schematic graph in the top right corner of Fig. 89). This kind of diagram can be considered as intermediate between the two considered above. The compound, unstable above the temperature t, decomposes before it reaches the melting point (peak c' on the dotted curve corresponds to it). Consequently, in such diagrams, curve ab showing freezing of component B is, as it were, moved onto curve ec' showing freezing of the compound.

Let us consider certain features of this diagram. It has two invariant points — eutectic point e and **peritectic** (transition) point d corresponding to the coexistence of three phases (the liquid solution and two solid phases — correspondingly A and D, and D and B). Consider cooling of the system whose points are to the right and above point d in the diagram. Mixture P cools as follows. At a temperature corresponding to point l', the solution will become saturated with substance B; when the temperature t is reached (point c), the ratio between the solid (g) and liquid (d) phases will equal

cd/*cg*. At this moment, the removal of the heat δQ causes the appearance of the first crystal of a new phase — the compound — because it is stable at this temperature. The system becomes invariant, which is characterized by stopping of the temperature change. A new phase (point *c*) is formed from the phases which points *d* and *g* correspond to, and the process of heat removal is compensated by the heat of the process

$$\text{Liquid solution } d + \text{B(c)} \rightarrow \text{D(c)}$$

Since the ratio between the amounts of the phases characterized by points *d* and *g* corresponds to the composition of the compound (point *c*), they disappear simultaneously. The result is that in Eq. (5.49) we have $f \neq 0$, i.e. the compound begins to cool.

If we take an unsaturated solution whose composition is between points *d* and *c*, its cooling will differ from the above in that at the moment when the temperature *t* is reached, the ratio between the amount of solution *d* and that of solid B will be greater than previously. Therefore, all the previously precipitated amount of B will be used up in forming compound D, and an excess of solution *d* will remain. Upon further cooling, the composition of the phases will change along lines *de* and *ck*, etc. This process is shown in Fig. 89 for the system H_2O-NaCl (see Example 3).

Conversely, if the mixture is richer in substance B than the compound, after freezing of the latter an excess of B(c) remains. Consequently, upon further cooling, solid D (line *ckD*) and B (line *gB*) will coexist; the ratio between them is determined according to the lever rule keeping in mind the position of the initial point.

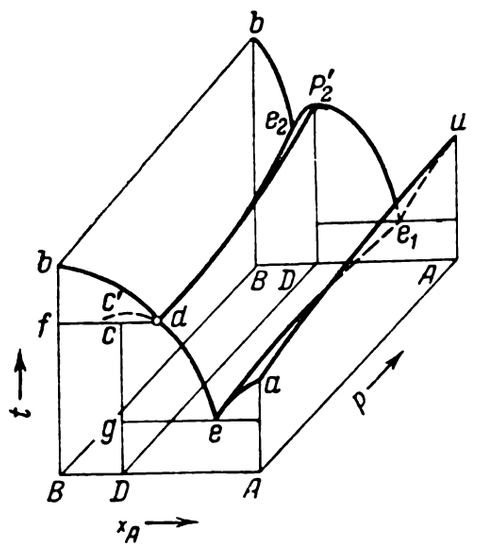

Fig. 90. Transition from a system with a hidden peak (see Fig. 89) to a system with an explicit peak (see Fig. 88)

In all the above cases, the compound is formed with a constant composition of solution *d*, because according to the phase rule the system is invariant, i.e. not only *p* and *t*, but also the concentration of the solution are constant.

Systems in which a liquid phase of a different composition is in equilibrium with a compound are called **incongruent.**

When several compounds are present, the diagram accordingly becomes more complicated.

Transition of the above system to one with a stable compound is shown schematically in Fig. 90 (this transition in the given case is associated with a change in the pressure).

Figure 91 shows a solubility diagram for the system $LiClO_3$-H_2O, which forms both a congruent and an incongruent compounds.

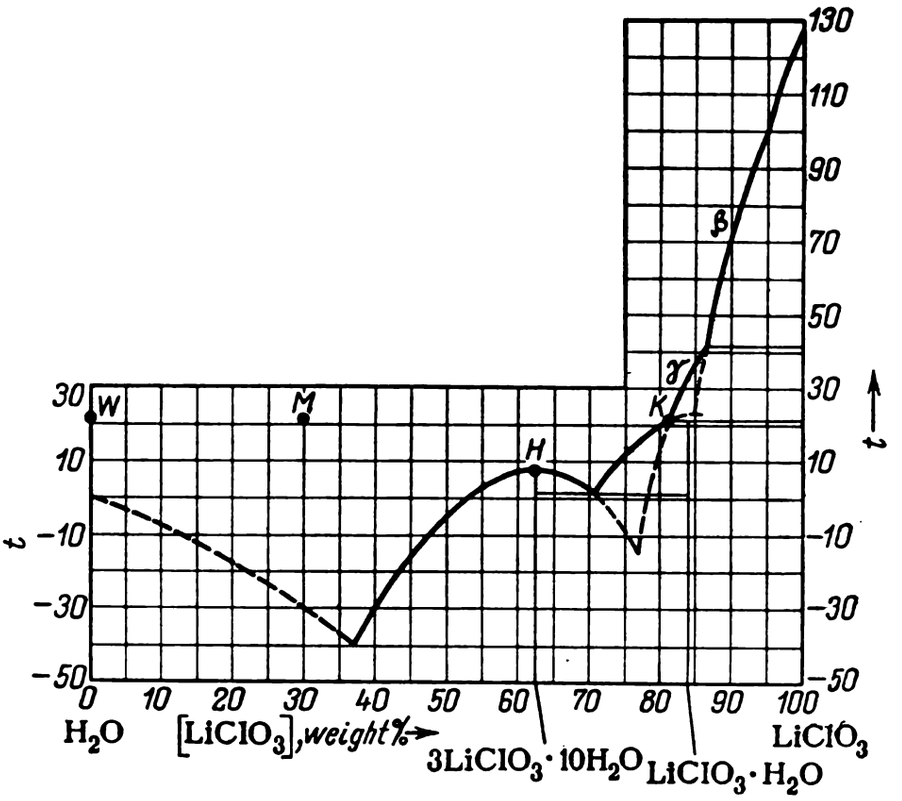

Fig. 91. Solubility diagram for the system $LiClO_3$-H_2O.
(See Example 4)

Example 3. One kilogram of a 28% solution of NaCl is cooled from 160 to −10 °C. Find the amount of precipitated salts (NaCl and $NaCl \cdot 2H_2O$) and the amount and composition of the final solution. Use the data given in Fig. 89 for the calculations (at point d_1 26.5% of NaCl, at point l_2 24.8% of NaCl).

Solution. The cooling process corresponds to straight line P_1m_2. At $t = 80$ °C (point l_1'), freezing out of NaCl begins. This will continue to $t = 0$ °C (point d_1). Let y stand for the amount of salt formed. It is obvious that

$$\frac{\text{NaCl}}{H_2O} = \frac{26.5}{73.5} = \frac{y}{720}$$

whence $y = 260$ g, i.e. 280 − 260 = 20 g of NaCl will precipitate.

Upon the further removal of heat, the formation of $NaCl \cdot 2H_2O$ begins (point c_1) and gradually all of the precipitated NaCl transforms into the crystallohydrate. The distribution of the solution components between the liquid and solid phases at the moment of complete transformation of the NaCl into $NaCl \cdot 2H_2O$ will be as follows:

280 g of NaCl $= k \times 26.5$ g of NaCl $+ z$ g of NaCl

720 g of H_2O $= k \times 73.5$ g of H_2O $+ w$ g of H_2O

the ratio between the components in the compound will be

$$\frac{\text{NaCl}}{2\text{H}_2\text{O}} = \frac{z}{w} = \frac{58.5}{36.0}$$

We find from these equations that $280 = 26.5k + z$ and $720 = 73.5k + 0.615z$, whence $k = 9.58$.

Consequently, the liquid phase (point d_1) will have a mass of $9.58 \times 100 = 958$ g and consist of $9.58 \times 26.5 + 9.58 \times 73.5 = 254$ g of NaCl + 704 g of H_2O.

The solid phase (point c_1) will have a mass of $z + w = 26 + 16 = 42$ g.

[If Fig. 89 were drawn to a larger scale, then the amount of solution and crystallohydrate could have been found directly from the diagram. Letting u stand for the mass of the crystallohydrate, in accordance with the lever rule we find $(1000 - u)/u = m_1c_1/m_1d_1$.]

After all the previously precipitated NaCl has transformed into $NaCl \cdot 2H_2O$, the latter begins to precipitate from the solution. At the moment when $t = -10\,°C$ is reached, the liquid phase will contain 24.5% of NaCl, and the distribution of the substances between the liquid and solid phases will be expressed by the equations

$$280 \text{ g of NaCl} = k' \times 24.5 \text{ g of NaCl} + z' \text{ g of NaCl}$$

$$720 \text{ g of } H_2O = k' \times 75.5 \text{ g of } H_2O + w' \text{ g of } H_2O$$

while the ratio between the components in the chemical compound will be given by the equation

$$\frac{\text{NaCl}}{2\text{H}_2\text{O}} = \frac{z'}{w'} = \frac{58.5}{36.0}$$

From these equations, we find $k' = 9.07$, $z' = 58$ g and $w' = 35.7$ g. Therefore, at $t = -10\,°C$ there remain 907 g of brine (222 g of NaCl and 685 g of H_2O), and the amount of precipitated crystallohydrate is 93 g.

It is obvious that $907/93 = s_2m_2/m_2l_2$.

Example 4. What amount of water has to be added to a mixture consisting of 100 g of a solution saturated at $t = 21\,°C$ and 500 g of $LiClO_3 \cdot H_2O$ to get a 30% solution?

Solution. In the solid phase there are

$$500 \times \frac{M_{LiClO_3}}{M_{LiClO_3 \cdot H_2O}} = 500 \times \frac{90.4}{108.4} = 417 \text{ g of } LiClO_3$$

and $500 - 417 = 83$ g of H_2O.

The liquid phase consists of 81 g of $LiClO_3$ and 19 g of H_2O (see Fig. 91, point K). Consequently, the mixture contains $417 + 81 = 498$ g of $LiClO_3$ (83%) and $83 + 19 = 102$ g of H_2O (17%). According to the lever rule

$$\frac{100 + 500}{y} = \frac{30}{83 - 30}$$

whence $y = 53 \times 600/30 = 1060$ g or 1.06 kg of H_2O.

9.1.3. Solution-Gas Equilibrium

If the solute is not volatile, i.e. the vapour of the pure solvent is in equilibrium with the solution, then the subscript i in Eq. (9.1) relates to the first component, and the numerator of the right-hand side of the equation equals the heat of condensation of the vapour into the *solution*. By dividing this quantity into the heat of condensation of the vapour into the pure solvent and the heat of reaction in the solution, and taking into account that the second addend is usually smaller than the first in absolute value, we conclude that $(\overline{H}_1 - H_1) < 0$, i.e. $(\partial x_1/\partial T) < 0$, and therefore $(\partial T/\partial x_2) > 0$. Consequently, the boiling point of a solution of a non-volatile substance is higher than that of the pure solvent. This conclusion also follows directly from the principle of displacement of equilibrium — the introduction of a non-volatile substance into an equilibrium one-component liquid-vapour system leads to diminishing of the solvent concentration in the liquid phase, which makes the vapour tend to condense (because this increases the concentration of the solvent lowered by the introduction of the second component); the temperature must be raised to restore the violated equilibrium. It should be borne in mind that the enthalpy of the solvent in equilibrium with the solution (H_1) generally differs from that of the vapour over the pure solvent, because the difference between the vapour pressures and the change in enthalpy upon isothermal compression may be disregarded only when the vapour is close in its properties to an ideal gas.

When the solvent is not volatile, i.e. a gas dissolved in a liquid (or in a solid) is in equilibrium with the solution and $i = 2$, the numerator of the right-hand side of Eq. (9.1) will equal the heat of condensation of the gas. The latter quantity is negative, which indicates diminishing of the solubility of the gas with increasing temperature. This does not hold for any temperature interval — the isobar $x_2 = \varphi(T)$ may have a minimum, which is connected with a change in the sign of $(\Delta H_{cond})_2$ (the position of the temperature minimum depends on the pressure, whose influence is not great). The presence of a minimum on the solubility isobar is due to the

fact that both components can mix in any proportion above the critical temperature of the solvent, i.e. a growth in solubility should be observed as the critical point is approached. Therefore, when the solubility drops with a growth in the temperature, the minimum of solubility should be sought at a higher temperature. Hence, the existence of a minimum on the isobars $x_2 = \varphi(T)$ is a general phenomenon and is not connected with the specific properties of the solvent and solute.

The relationship between the temperature and composition of an ideal solution is determined by Eq. (9.2). For $i = 1$, the numerator of the right-hand side of the equation equals the heat of condensation of the solvent, and for $i = 2$ it equals the heat of condensation of the solute.

The following equation holds for an infinitely dilute solution:

$$\left(\frac{\partial T}{\partial x_2}\right)_p = \frac{-R(T_b)_1^2}{(\Delta H_{cond})_1} \tag{9.6}$$

It is similar to Eq. (9.5). The difference is that the right-hand side of Eq. (9.6) is positive ($\Delta H_{cond} < 0$), i.e. the boiling point of the solution of a non-volatile substance is higher than that of the solvent. The proportionality factor is called the **ebullioscopic * constant.** Considerations similar to those set out on p. 291 for the cryoscopic constant are valid for it.

9.2. RELATIONSHIP BETWEEN PRESSURE AND CONCENTRATION

Assume that the pressure changes isothermally by dp when a solution and a pure component are in equilibrium. Equilibrium will be restored as a result of a change in the concentration of the solution. This means that

$$\left(\frac{\partial G_i}{\partial p}\right)_T dp = \left(\frac{\partial \overline{G}_i}{\partial p}\right)_{T, x_i} dp + \left(\frac{\partial \overline{G}}{\partial x_i}\right)_{p, T} dx_i$$

or by Eqs. (5.25) and (8.6)

$$V_i\, dp = \overline{V}_i\, dp + \left(\frac{\partial \overline{G}_i}{\partial x_i}\right)_{p, T} dx_i$$

After transformations, we get

$$\left(\frac{\partial x_i}{\partial p}\right)_{T, eq} \quad \frac{V_i - \overline{V}_i}{(\partial \overline{G}_i/\partial x_i)_{p, T}} \tag{9.7}$$

* From the Latin "ebullire" — to bubble or boil and the Greek "skopein" — to look.

Equation (9.7) can be found directly from Eqs. (8.21), which in this case (T = const, $x_i'' = 1$) become

$$\left.\begin{aligned}(V_1 - \overline{V}_1)\,dp + x_2\left(\frac{\partial^2 G}{\partial x_2^2}\right)dx_2 = 0\\ (V_2 - \overline{V}_2)\,dp - x_1\left(\frac{\partial^2 G}{\partial x_2^2}\right)dx_2 = 0\end{aligned}\right\}$$

whence Eq. (9.7) follows in accordance with Eq. (8.20). Equation (9.7), like Eq. (9.1), finds no practical use, since *in the general case* the dependence of G_i on x_i is unknown.

In accordance with the principle of displacement of equilibrium, the nature of the dependence of x_i on p is determined by the sign of the quantity $V_i - \overline{V}_i$, which, in turn, depends on the properties of the pure component, the compressibility of the solvent, the nature and concentration of the solution.

9.2.1. Solution-Solid Component Equilibrium

If we represent the quantity $\Delta V_i = V_i^c - \overline{V}_i$ in the form

$$[V_i^{(lq)} - \overline{V}_i] - [V_i^{(lq)} - V_i^c]$$

where $V_i^{(lq)}$ is the volume of the supercooled pure component, then it becomes obvious that the sign of $\partial x_i/\partial p$ is determined by that of $V_i^{(lq)} - V_i^c$, because as a rule the quantity $V_i^{(lq)} - \overline{V}_i$ is negligible.

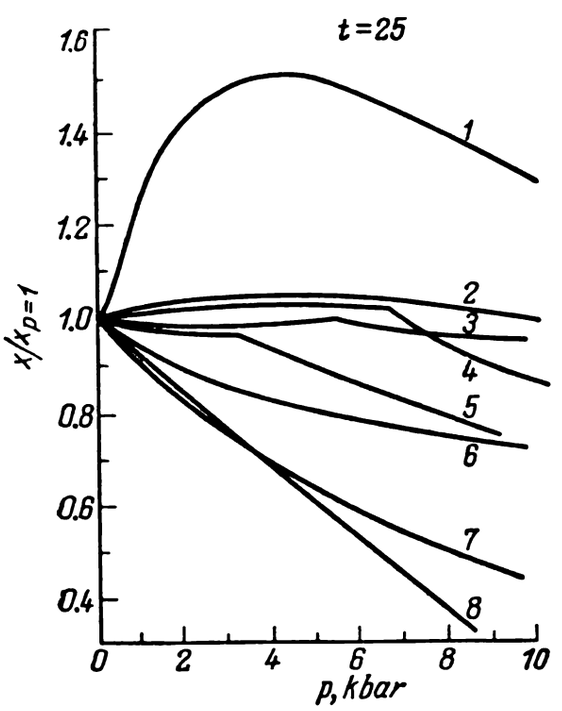

Fig. 92. Change in relative solubility of selected salts in water depending on the pressure:
1 – K_2SO_4; 2 – NaCl; 3 – $CdSO_4$; 4 – $ZnSO_4$; 5 – $CdCl_2$; 6 – $CdBr_2$; 7 – NH_4NO_3; 8 – CdI_2

In general, the solubility of solids and liquids depends only slightly on the pressure; the numerator of the right-hand side of Eq. (9.7) is not great for them. To achieve a considerable change in the solubility, the solute has to be dissolved at a very high pressure. This can be seen directly from Fig. 92. For K_2SO_4, NaCl, NH_4NO_3 and CdI_2 the numerator of the right-hand side of Eq. (9.7) is the difference between the molar volume of the solid salt and its partial molar volume in a saturated solution; for the other salts it equals the quantity $(V^c_{\text{salt}\cdot n\text{H}_2\text{O}} - \overline{V}_{\text{salt}} - nV_{\text{H}_2\text{O}})$,

because these salts form crystallohydrates ($CdSO_4 \cdot \frac{8}{3} H_2O$, $ZnSO_4 \cdot 7H_2O$, $CdCl_2 \cdot 2\frac{1}{2} H_2O$ and $CdBr_2 \cdot 4H_2O$, respectively). For the last three substances, there are discontinuities on the curves due to phase transitions in the crystallohydrates which cause a stepwise change in their molar volumes.

For an ideal solution, general equation (9.7) in accordance with Eq. (8.44) becomes

$$\left(\frac{\partial \ln x_i}{\partial p}\right)_T = \frac{V_i^c - V_i^{(lq)}}{RT} \tag{9.8}$$

Although in an ideal solution $\overline{V}_i = V_i$ (Eq. 8.38), this does not mean that the solubility in it is independent of the pressure, because the partial molar volume of the solute equals its molar volume not in the solid, but in the supercooled liquid state.

For calculations by Eq. (9.8) within a comparatively broad interval of pressures we may consider that $\Delta V \approx$ const; it is good to take the solubility at $p = 1$ atm as the lower limit of integration.

9.2.2. Solution-Gas Equilibrium

When writing down the difference $V_2^g - \overline{V}_2$ in the form $[V_2^{(lq)} - \overline{V}_2] - [V_2^{(lq)} - V_2^g]$, it becomes obvious that the sign of the left-hand side of Eq. (9.7) is determined by the sign of $V_2^{(lq)} - V_2^g$. For the usual pressures, this difference is negative and very great in absolute value. Therefore, an increase in pressure is attended by a considerable increase in the solubility of a gas. With a growth in pressure, the quantity ΔV will diminish, and the relative increase in solubility will lower. At high pressures, when the volumes V_2^g and $\overline{V}_2$ become commensurable, a peak will appear on the isotherm $x_2 = \varphi(p)$ (see below). Its position in accordance with Eq. (9.7) will be determined by the condition $\overline{V}_2 = V_2^g$ (for high pressures the influence of the pressure on $\overline{V}_2$ must also be taken into consideration).

Solubility of Gases in Liquids under Pressure. If a solution is ideal at all concentrations and if the temperature at which a gas dissolves is higher than its critical temperature, then the value of the saturated vapour pressure p_i° in Eq. (8.45) loses its meaning, and for calculating the solubility it becomes necessary to extrapolate the value of $p_i^\circ = \varphi(T)$ to the region of above-critical temperatures. Such extrapolation is conducted according to a graph of log p against T^{-1}, and although it has a conditional nature, it gives reliable results. This is indicated by the coincidence of calcu-

lated and experimentally found data for solvents with higher critical parameters.

Equation (8.51) gives an error of from 1 to 3 per cent for a number of gases (and gas mixtures) even at pressures below 1 atm, while for pressures of several scores of atmospheres it gives quite inaccurate results. The deviations from Eq. (8.51) generally diminish with elevation of the temperature because of the lower ability of the gas to react with the solvent. But to apply Henry's law for the region of high pressures, it is not sufficient to substitute the fugacity for the pressure. Moreover, Eq. (8.51) gives better results than Eq. (8.50) for high pressures. This is illustrated by Fig. 93.

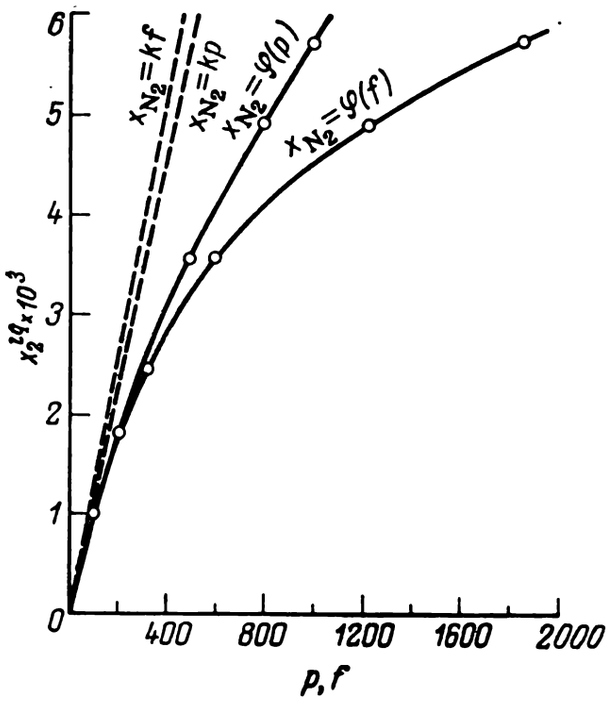

Fig. 93. Solubility of nitrogen in water under pressure ($t = 25$ °C).

Checking of Eqs. (8.50) and (8.51)

I. Krichevsky and his assistants were the first to quantitatively consider the solubility of a poorly soluble gas in a liquid under a high pressure (see [B60]). They showed that two errors are usually made when interpreting experimental data. The first is that investigators forget that Henry's law is applicable only to infinitely dilute solutions.

With gas mixtures, the concentration of a component can be changed without changing the pressure, but with liquid and solid solutions a change in x_2 inevitably causes the pressure to change. It was considered for a long time that Henry's coefficient depends only on the temperature, and therefore a natural discrepancy appeared between the experimental data and the quantities found by the equation $p_2^g = \varphi(T)x_2^{lq}$ or $f_2^g = \varphi(T)x_2^{lq}$. Thus, the second error is the assumption that Henry's coefficient does not depend on the pressure: for high pressures this assumption is groundless.

Equation (8.50) is accurate only when the concentration changes isobarically. If the pressure changes within considerable limits, this equation has to be applied in a different form (see below).

Example 5. Find the solubility of methane at $p = 1$ atm and $t = 25$ °C in a solvent which it forms an ideal solution with.

Solution. Since $t = 25$ °C corresponds to a temperature above the critical one for CH_4 (see Appendix 9), for our calculations we extrap-

olate the experimental data according to the temperature dependence of the saturated vapour pressure to $1/T = 1/(273.2+25) = 0.00335$ and get the fictitious value of $p \approx 370$ atm. Hence the solubility of methane in any solvent, when its partial pressure over the solution equals 1 atm, will be, according to Eq. (8.51), $x^{lq}_{meth} = 1/370 = 0.00276$, which corresponds to experimental data (in xylene, for example, $x^{lq}_{meth} = 0.0026$, in hexane $x^{lq}_{meth} = 0.0031$, etc.).

Solubility of a Pure Gas. Assuming when deriving Eq. (9.7) that $\bar{V}_2\, dp = RT\, d \ln f_2$ and using Eq. (8.44), we get $RT\, d \ln f_2 = \bar{V}_2\, dp + RT\, d \ln x_2$. Assuming that the quantity $\bar{V}_2$, which we shall call the *apparent* partial molar volume at $x_2 = 0$ (the meaning of this term will become clear on a later page), does not depend on the composition of a solution, and considering that $\bar{V}_2 \neq \varphi(p)$, we shall integrate this equation within the limits from p° to the total pressure p (and accordingly from 0 to x_2). Hence, taking into consideration Eq. (8.50), we get the **Krichevsky-Kazarnovsky equation** (1935)

$$\ln \frac{f_2^g}{x_2^{lq}} = \ln k' + \frac{\bar{V}_2(p - p_1^\circ)}{RT} \tag{9.9}$$

where f_2^g and x_2^{lq} are taken on condition of equilibrium, i.e. at the pressure p and temperature T, and k' is Henry's coefficient at p_1°.

The Solvent Has an Insignificant Vapour Pressure. In this case, the quantity f_2^g may be identified with the fugacity of a pure gas at the pressure p, and the quantity p_1° may be disregarded. Equation (9.9) thus becomes

$$\ln \frac{(f_2^g)^\circ}{x_2^{lq}} = \ln k' + \frac{\bar{V}_2 p}{RT} \tag{9.10}$$

It follows from Eqs. (9.9) and (9.10) that the solubility of a gas can be calculated according to the values of the apparent partial molar volume of the gas in a solution, Henry's coefficient and the fugacity of the gas at a given pressure. Conversely, if we know the relationship $x_2^{lq} = \varphi(p)$, then the quantities k' and $\bar{V}_2$ can be found from a graph of $\ln [(f_2^g)^\circ / x_2^{lq}]$ against p (Fig. 94*a*).

Consider the solubility of a gas (X_2) in a metal under pressure if the gas dissociates upon solution. Since the solubility of a gas in a metal is insignificant, we may assume that an infinitely dilute solution is formed. Upon equilibrium, we have $G_{X_2} = 2\bar{G}_X$, because the gaseous phase is practically a pure gas. Hence by Eq. (9.10)

$$\ln \frac{\sqrt{f_{X_2}^g}}{x_{X_2}^g} = \ln k' + \frac{\bar{V}_X^c p}{RT}$$

At comparatively low pressures and high temperatures, we have $f^g_{X_2} \approx p_{X_2}$; besides, $\bar{V}^g_X \approx 0$, and hence $x^g_{X_2} = k''\sqrt{p}$, i.e. the solubility of a gas in a metal is proportional to $\sqrt{p}$.

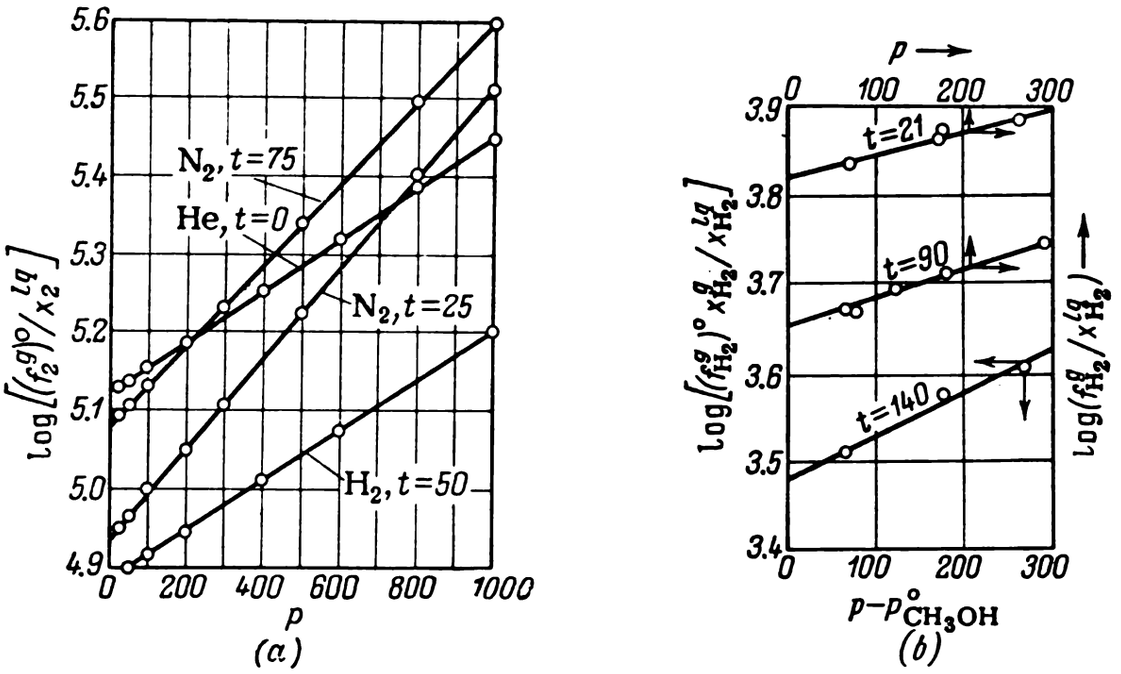

Fig. 94. Solubility of gases in water under pressure:
a—checking of Eq. (9.10) (see Example 7); *b*—checking of Eqs. (9.10) and (9.11) (see Example 8)

When we took into account the dependence of $\bar{G}_2$ on p in deriving Eq. (9.9), we thus took into account the dependence of Henry's coefficient on the pressure. Therefore, the main error preventing the substantiation of the solubility of gases under pressure was the assumption that pressure affects $\bar{G}_2$ only through the concentration of a gas. Ignoration of the direct influence of p on $\bar{G}_2$ results in Eq. (8.50), which contradicts experimental data and holds only when the concentration changes at constant pressure.

For low pressures, when f^g_2 is very small and $p\bar{V}_2/RT \approx 0$, the derived equations transform directly into Eq. (8.51). Therefore k' in Eq. (9.10) coincides with k in Eq. (8.51). It is not altogether correct, however, to state on this basis that Henry's law in the form of Eq. (8.51) holds up to a certain pressure, since this does not disclose its essence as a law true only for infinitely dilute solutions. Investigation of the limits of the applicability of Henry's law should consist in determining the corresponding limiting *concentration* of a solution. The establishment of the pressure corresponding to this limit is a secondary problem mainly for convenience.

Since the dissolving of a gas in a liquid at low vapour pressures is the most widespread case in practice, preference should be given to Eq. (9.10). Its use for calculating solubility gives good coincidence with experimental results, notwithstanding the fact

that in deriving this equation the dependence of $\bar{V}_2$ on p was not taken into consideration because of the absence of sufficient experimental data.

For very high pressures, we cannot ignore the dependence of $\bar{V}_2$ on p. It is impossible to predict its nature, but its very existence underlies the possibility of a peak appearing on the curve of x_2 against p, which does not follow from Eqs. (8.50) and (8.51). This led to the erroneous opinion that the solubility of a gas must continuously grow with increasing pressure even at very high pressures (at $T = \text{const}$).

The changes in the volumes of the gas and the liquid become commensurable at very high pressures, and therefore the volume of the liquid must not be ignored.

Thus, if we dissolve one mole of nitrogen at $p = 1$ atm ($t = 25°C$) in a very great amount of water, its volume will grow by $\bar{V}_2 = 40$ cm^3, while the volume of the gaseous phase will diminish by $V_2 \approx$ $\approx 24\,400$ cm^3; at $p = 1000$ atm we have $\bar{V}_2 \approx 40$ and $V_2 = 48.8$ cm^3; if $p = 6000$ atm, then $\bar{V}_2 \approx 40$ and $V_2 = 28.8$ cm^3. Thus, at $p = 1$ and $p = 1000$ atm, the solubility grows with the pressure, whereas for $p = 6000$ atm, despite the widespread viewpoint, but in accordance with the principle of displacement of equilibrium (solution is attended by an increase in volume!), it diminishes. The peak of solubility, falling to the pressure at which solution is not accompanied by a change in volume, is not always in the region of very high pressures. (For example the solubility of nitrogen in ethyl ether at 25 °C reaches a maximum at from 500 to 550 atm.) The greater the value of $\bar{V}_2$, the lower is the pressure at which the peak is observed.

Example 6. How can we explain that for high pressures Eq. (8.51) gives better coincidence with experimental results than Eq. (8.50) if in the cases studied $\bar{V}_2^{lq} > 0$ and $f > p$?

Solution. For $\bar{V}_2^{lq} > 0$, in view of Eq. (9.10), the solubility of a gas is found to be lower than should be expected on the basis of Eq. (8.50). At the same time, since the fugacity is greater than the pressure, the solubility of a gas should grow more rapidly with increasing pressure than follows from Eq. (8.51).

Example 7. Check the correctness of Eq. (9.10) on the basis of the following experimental data on the solubility of nitrogen in water at 25 °C:

p	25	50	100	200	300	500	800	1000
$x_{N_2}^{lq} \times 10^3$	0.280	0.542	1.015	1.812	2.455	3.558	4.909	5.720

Show that the above data do not satisfy Eq. (8.50).

Solution. We find the fugacity of nitrogen at the indicated pressures in Fig. 40. Next we plot a graph of log $(f^{g}_{nit}/x^{lq}_{nit})$ against pressure (Fig. 94*a*), according to which by Eq. (9.10) we find the apparent partial molar volume $\bar{V}_2^{lq} = 2.303RT \tan \alpha = 32.8$ (the partial molar volume according to experimental data was found equal to 40 cm³). The coefficient of Eq. (9.10) is $k' = 8.576 \times 10^4$ instead of 8.467×10^4 and 8.773×10^4 found experimentally at low pressures ([D4], **5** : 413). Hence, for the given case we have log $(f^{g}_{nit}/x^{lq}_{nit}) = 4.933 + 0.000\,581\,3p$.

Should we process the above data with the aid of Eq. (8.50), we get the graph shown in Fig. 93. The same figure shows data corresponding to Eq. (8.51), which give a relatively better coincidence. Neither of these two equations corresponds to the experimental data for high pressures.

The Solvent Has a High Vapour Pressure. If a gas is dissolved in a liquid having a high vapour pressure (here belong solutions of gases in liquid ammonia, liquid air, etc., in many organic solvents and also in water at a high temperature), then Eq. (9.9) should be used for calculations.

Therefore, when the saturated vapour pressure of the solvent becomes appreciable, its presence in the gaseous phase must no longer be ignored. For the same reason, f_2 may not be identified with the fugacity of the pure gas at the given pressure, i.e. the value of the fugacity of a component of a gas mixture must be used. Nevertheless, before passing from a less accurate equation to a more accurate one, it is necessary to establish what is greater in the given specific conditions — the error in using Eq. (9.10), or the error in determining the solubility.

We can use the fugacity rule (see Sec. 8.4) to calculate the fugacity of a gas f_2 in the vapour phase if we assume that the gas mixture is an infinitely dilute solution (an assumption that is justified when the gas predominates in the mixture). In this case, Eq. (9.9) becomes

$$\ln \frac{f_2^{\circ} x_2^{g}}{x_2^{lq}} = \ln k' + \frac{\bar{V}_2^{lq}(p - p_1^{\circ})}{RT} \qquad (9.11)$$

where f_2° = fugacity of the pure gas at a pressure equal to the total pressure over the solution

x_2^{g} = mole fraction of the gas in the vapour phase.

Equation (9.11) gives good coincidence with experimental results, which can be seen in Fig. 94*b* (the isotherm $t = 140$).

The two equations (9.9) and (9.11) also transform into Eq. (8.50) when $\bar{V}_2^{lq} = 0$, and not only when $p = p_1^{\circ}$, but the second term

of the right-hand side has to be taken into account even if the difference in pressures $p - p_1^\circ$ is relatively small (of the order of magnitude of a score of atmospheres).

Unlike Eq. (9.9), Eq. (9.11) stops being correct when the total pressure approaches the saturated vapour pressure of the solvent: if the gas does not predominate considerably over the solvent vapour, then Eq. (8.50) gives great errors. I. Krichevsky proposed the following equation for this case (its derivation is omitted):

$$\frac{k^{lq}}{k^g} = \frac{(V_1^g)^\circ - (V_1^{lq})^\circ}{RT}\left(\frac{\partial p}{\partial x_2^{lq}}\right)_{eq,\ T} + 1 \qquad (9.12)$$

where k^{lq} and k^g = Henry's coefficients for the gas in the liquid and gaseous phases

$(V_1^g)^\circ$ and $(V_1^{lq})^\circ$ = molar volumes of the solvent in the gaseous and liquid states at its saturated vapour pressure

$(\partial p/\partial x_2^{lq})_{eq,\ T}$ = derivative of the pressure with respect to the mole fraction of the gas dissolved in the liquid at $x_2^{lq} = 0$.

In conclusion, we must indicate that great discrepancies were discovered between the experimental values of $\bar{V}_2^{lq}$ and those calculated by Eq. (9.9): in all the investigated cases except one (a solution of CH_4 in H_2O), the true partial molar volumes were greater than the calculated ones. Therefore, account had to be taken of the dependence of $\bar{V}_2^{lq}$ on x_2^{lq}, which had been disregarded when deriving Eq. (9.9). Although the resulting equation [derived by I. Krichevsky and A. Ilyinskaya (1945)] was found to be accurate in all respects, Eq. (9.9) or (9.10) will be quite sufficient for determining the *solubility* of a gas at a high pressure, because the calculation of solubility by these equations gives good coincidence with experimental data (see Fig. 94*a*).

Example 8. In investigating the solubility of hydrogen in methanol, the following results were obtained:

$t = 21$	p		76	178	179	272
	H_2/CH_3OH, cm³/g		8.11	19.5	19.7	29.7
$t = 90$	p	71	74	134	186	300
	H_2/CH_3OH, cm³/g	11.1	11.7	20.6	29.2	46.5
$t = 140$	p			78	196	281
	H_2/CH_3OH, cm³/g			16.0	36.9	57.7

The error of measurements is estimated to be 1-3%. Use these data to calculate the values of Henry's coefficients and the apparent partial molar volumes of hydrogen in a methanol solution.

Solution. The saturated vapour pressures of CH_3OH at these temperatures equal 0.157, 2.494 and 10.63 atm, respectively ([D4], 5 : 370, 395). If using Eq. (9.10) for 21 and 90 °C introduces an error not exceeding the experimental errors, then for 140 °C the saturated vapour pressure of the methanol is great, and it would be a mistake to ignore its presence in the gaseous phase. Therefore, Eq. (9.11) should be used in the calculations for 140 °C.

Computing the values of f_{H_2} for the above conditions and plotting the values of $\log (f^g_{H_2}/x^q_{H_2})$ for 21 and 90 °C on a graph against p, and the values of $\log [(f^g_{H_2})^\circ x^g_{H_2}/x^{lq}_{H_2}]$ against $p - p^\circ$ for 140 °C, we get straight lines (see Fig. 94*b*) from whose position we determine the values of k and $\bar{V}^{lq}_{H_2}$:

t	21	90	140
k	6760	4410	2970
$\bar{V}^{lq}_{H_2}$	12.1	26.0	40.5

Solubility of a Gas Mixture Component. Assuming as previously that the solution being investigated retains the properties of an infinitely dilute solution, we shall write down the condition of equilibrium for the i-th component of a gas mixture : $G_i = \bar{G}_i$.

If we assume that the gases do not react with one another in the solution, then the partial molar Gibbs energy of each component will depend only on its concentration and on the total pressure over the solution. Hence Eq. (9.9) and all the subsequent reasoning relating to it remain in force. For the same reason in the case of a solvent with a low saturated vapour pressure, assuming that $\bar{V}^{lq}_i \neq \varphi(p)$, we also get a semi-empirical equation similar to Eq. (9.10)

$$\ln \frac{f^g_i}{x^{lq}_i} = \ln k_i + \frac{\bar{V}_i{}^q p}{RT} \tag{9.13}$$

where f^g_i = fugacity of a component in the gaseous phase
x^{lq}_i = its mole fraction in the solution
p = total pressure.

Although we may assume that $\bar{V}^{lq}_i$ and k_i have the same values as for a pure gas, in the general case (Krichevsky, Ilyinskaya) the apparent partial molar volume upon the simultaneous solubility of gases does not coincide with this quantity for a pure gas.

It follows from Eq. (9.13) that the solubility of a component of a gas mixture (at $\bar{V}^{lq}_i > 0$) is less than that of the pure gas, because at the same fugacities of the pure gas and the gas in the mixture the pressure of the latter is greater than the pressure of the pure gas.

If the fugacity of a gas in a mixture can be calculated according to the fugacity rule, then in accordance with Eq. (9.9) the solubility of the gas from the mixture is

$$x_i = (x_i^{lq})^\circ \, x_i^g \tag{9.14}$$

where $(x_i^{lq})^\circ$ = solubility of the pure gas

x_i^g = its mole fraction in the gas mixture.

Should the total pressure of a gas mixture equal the pressure of a pure gas, then by Eqs. (9.10) and (9.13) we have

$$\frac{(x_i^{lq})^\circ}{x_i^{lq}} = \frac{(f_i^g)^\circ}{f_i^g} \tag{9.15}$$

where $(x_i^{lq})^\circ$ and x_i^{lq} = solubilities of the pure gas and the gas from the mixture

$(f_i^g)^\circ$ and f_i^g = corresponding fugacities.

When a gas mixture dissolves in a liquid with a great saturated vapour pressure, the calculations should be performed using an equation similar to Eq. (9.11).

A solubility peak is also observed when a gas mixture dissolves in a liquid (at the pressure when the partial molar volume of the component in the gaseous phase becomes equal to its partial molar volume in the liquid phase).

If the solutes react with one another, then

$$d\bar{G}_i = \left(\frac{\partial \bar{G}_i}{\partial p}\right)_{T,\, x} dp + \sum \left(\frac{\partial \bar{G}_i}{\partial x_i^{lq}}\right)_{p,\, T} dx_i^{lq}$$

i.e. the partial molar Gibbs energy at a constant temperature depends not only on the total pressure and the concentration of the given gas, but also on the concentration of the other gases in the liquid phase.

Integration of this equation yields a semi-empirical equation similar to Eq. (9.10):

$$\ln \frac{f_i^g}{x_i^{lq}} = \ln k_i + \frac{\bar{V}_i^{lq} p}{RT} + \frac{1}{RT}\left[\int_0^{x_2^{lq}} \frac{\partial \bar{G}_i}{\partial x_2^{lq}} dx_2^{lq} + \int_0^{x_3^{lq}} \frac{\partial \bar{G}_i}{\partial x_3^{lq}} dx_3^{lq} + \ldots \right] \tag{9.16}$$

In the absence of a reaction between the gases in a solution, it transforms into Eq. (9.13).

Thus, the difference between the solubility of a component of a gas mixture and its solubility in the pure state is in general due to three factors: (1) the influence of pressure; (2) the mutual influence of the mixture components; and (3) the mutual influence of the dissolved components. The first two factors are taken into

account by Eq. (9.13) and the last one by Eq. (9.16); ignoring them may lead to erroneous results. Calculations on the assumption that the solubility of a gas from a mixture equals the solubility of the pure gas at its partial pressure may lead to still greater errors. This approximation gives unsatisfactory results and may be used only for low pressures and when the mole fraction of a component in the gaseous phase is close to unity.

In general, if solution is attended by an increase in the volume of the liquid, then at an identical partial pressure the solubility is the lower, the greater is the total pressure.

Example 9. A mixture consisting of 80% of H_2 and 20% of CO_2 is purified of the carbon dioxide with the aid of water at $t = 25\,^\circ C$ and $p = 100$ atm. Find the amount of water needed per 1000 m^3 of hydrogen if the solubilities of CO_2 and H_2 in H_2O from the mixture in the above conditions are 10.8 and 1.20 m^3 per m^3 of H_2O, respectively. Assume that the water is saturated with the carbon dioxide up to 80%. For comparison, perform the calculations using Dalton's law.

The experimental data on the solubility of CO_2 and H_2 in H_2O at 25 °C can be expressed with the aid of the equations

$$V^{lq}_{CO_2} = 0.755p - 0.0042p^2 \text{ st. } m^3 \text{ per } m^3 \text{ of } H_2O$$

$$V^{lq}_{H_2} = 0.0244 + 0.017\,12p - 0.000\,001\,96p^2 \text{ st. } m^3 \text{ per } m^3 \text{ of } H_2O$$

Solution. Every 1000 m^3 must absorb $1000 \times 20/80 = 250$ m^3 of CO_2, which corresponds to a consumption of water of $250/10.8 \times \times 0.8 = 28.9$ m^3. A maximum of $28.9 \times 1.20 = 34.7$ m^3 of hydrogen, or $34.7 \times 100/1000 = 3.47\%$ is lost with this amount of water.

We shall perform the same calculations on the assumption that the solubility of a gas from a mixture equals the solubility of the pure gas at its partial pressure. From the equation given in the initial conditions of the example, we find that at $p_{\text{carb.diox.}} = = 0.20 \times 100 = 20$ atm the volume of the dissolved carbon dioxide is 13.42 m^3 per m^3 of H_2O, which corresponds to a consumption of water of $250/13.42 \times 0.8 = 23.3$ m^3. Similarly, for hydrogen we find a solubility equal to 1.38 m^3 per m^3 of H_2O, which corresponds to a loss of hydrogen of $23.3 \times 1.38 = 32.2$ m^3, or $32.2 \times \times 100/1000 = 3.22\%$. The results show that this method of calculations gives an error in the consumption of water over 19%. It should be taken into account here that the error is somewhat understated, because the errors in the values of the consumption of water and the solubility are opposite in sign and partly compensate each other.

It follows from the results of the calculations that when washing is conducted under a high pressure, the consumption of water

diminishes to a smaller extent than should be expected. This is connected with the fact that the calculation of the solubility of gases from gas mixtures according to the partial pressures always gives an overstated result (see Fig. 93).

9.3. GAS MIXTURE-PURE COMPONENT EQUILIBRIUM

When considering the influence of external pressure on saturated vapour pressure (see Sec. 7.5), it was mentioned that in practice account must be taken of an additional effect — the dissolving of the vapour of the condensed phase in the compressed gas.

In this connection, we shall consider the laws followed by the equilibrium between a pure substance and a vapour and gas mixture. We shall assume for simplification that the condensed phase is a pure component and the gaseous phase is an infinitely dilute solution. This assumption not only allows us to perform calculations, but in the first approximation corresponds to actual conditions, because an inert gas may be considered as insoluble, and the concentration of the vapour in the compressed gas is comparatively small. Hence in accordance with Eq. (9.7), the pressure dependence of the solubility of a substance in a gas will be expressed by the equation

$$\left(\frac{\partial \ln x_1^g}{\partial p}\right)_T = \frac{V_1 - \bar{V}_1^g}{RT} \tag{9.17}$$

An analysis of this equation gives the following results. The isotherm $x_1^g = \varphi(p)$ begins at $p = p_1^\circ$, when $x_1^g = 1$. It further drops, and quite sharply, because at low pressures $\bar{V}_1^g \gg V_1$. A subsequent increase of the pressure causes the rate of lowering of the solubility to slow down, since the value of $\bar{V}_1^g$ rapidly diminishes with V_1 remaining practically constant. At the pressure when $\bar{V}_1^g$ coincides with V_1, the curve will pass through a minimum. The corresponding pressure will be the greater, the smaller is V_1. Therefore, for example for solutions of water vapour in compressed nitrogen or compressed hydrogen, the minimum will set in at pressures greatly exceeding $p = 1000$ atm, whereas for solutions of organic liquids in compressed gases this is observed at considerably lower pressures [for example for solutions of CCl_4(lq) in N_2(g) at $p \approx 100$]. If at a low value of V_1, the minimum of the solubility occurs at comparatively low pressures, this means that the transition of the substance to the gaseous phase is attended by great compression, when the values of $\bar{V}_1^g$ are low [for example for solutions of H_2O(lq) in CO_2(g) because of great electrostriction caused by solution]. A further growth in pressure after the minimum has been passed will lead in the long run to an increase in $\bar{V}_1^g$, because the forces of repulsion begin

to tell at high pressures. Consequently, the curve $x_2 = \varphi(p)$ will gradually approach a horizontal line.

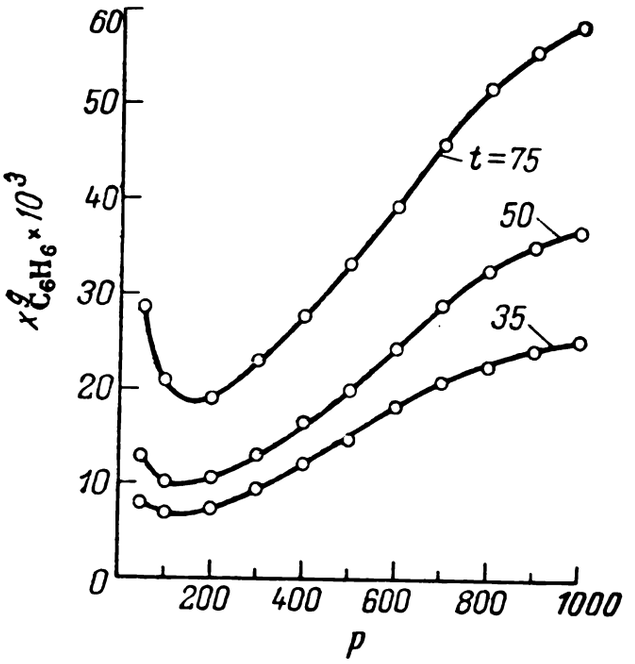

Fig. 95. Solubility of benzene vapour in compressed nitrogen

The general shape of a solubility curve is shown in Fig. 95 for a solution of benzene vapour in compressed nitrogen.

I. Krichevsky and his assistants carried out interesting studies on the theory of solubility of substances in compressed gases [B60]. Krichevsky and N. Khazanova succeeded in establishing an approximate semi-empirical relationship for the solubility of a polar substance in a non-polar gas. The presence of an inflection on the rising branch of the solubility isotherm was confirmed by Krichevsky and D. Gamburg.

9.4. INFLUENCE OF DISPERSION ON SOLUBILITY

In the same way as the diminishing of the size of drops causes the vapour pressure to grow, so does the diminishing of the size of crystals cause their solubility to increase. If we consider that the tendency of molecules of a liquid to pass into the vapour phase is similar to the tendency of molecules of a solid phase to pass into a solution, then we can use Eq. (7.42), substituting the mole fractions for the pressures in it. We thus get the equation

$$\ln \frac{x_2'}{x_2} = \frac{2\sigma}{RTr\rho} \tag{9.18}$$

where x_2' = solubility of the small crystals
x_2 = solubility of large crystals
σ = surface tension on the solid-solution interface
r = radius of the small crystals
ρ = density of the crystals.

Equation (9.18) gives only an approximate dependence of the solubility on the dispersion, since it takes no account of the heterogeneity of different portions of a surface and assumes that the surface tension does not depend on the radius of a crystal. In addition, the values of the surface tension for solids are not always sufficiently reliable.

Chapter 10

SOLUTION-SOLUTION EQUILIBRIUM IN BINARY MIXTURES

10.1. LIQUID-GAS EQUILIBRIUM FOR COMPLETELY MISCIBLE LIQUIDS AT LOW PRESSURES

10.1.1. Ideal Solution-Mixture of Ideal Gases

The gaseous phase may be considered as a mixture of ideal gases if a solution is under a low pressure and in accordance with Dalton's law

$$p = p_1 + p_2 \quad \text{or} \quad p_i = px_i^g \tag{10.1}$$

where p = total pressure of the mixture
p_i = partial pressure of the corresponding substance.

From Eq. (8.45), the partial pressure of a component of an ideal solution is proportional to its concentration. Hence for each temperature, the dependence of the partial and total pressures on the composition of a solution is expressed by straight lines [see Fig. 96 (the lines showing the partial pressure are depicted only for $t = 36.1\,°C$)].

Combining Eqs. (8.45) and (10.1), we get the equation

$$p_i = p_i^\circ x_i^{lq} = px_i^g \tag{10.2}$$

by means of which, setting the composition of the liquid phase, we can easily find the composition of the vapour phase if we know p_1° and p_2° (this is shown in Fig. 97, where one of the isotherms of Fig. 96 is reproduced *).

The ratio

$$\frac{x_i^g}{x_i^{lq}} = \frac{p_i^\circ}{p} = K_i \tag{10.3}$$

characterizing the distribution of a given substance between phases is called the **phase equilibrium constant (distribution constant** or **equilibrium ratio).**

Expressing the difference in the composition of coexisting phases at given p and T by means of the equation

$$\frac{x_1^g}{x_2^g} = \frac{x_1^{lq}}{x_2^{lq}} \frac{p_1^\circ}{p_2^\circ} \tag{10.4}$$

* Here and in the following, the curves showing the composition of a vapour are depicted by dashed lines.

we see that if $p^\circ > p_2^\circ$, then $x_1^g > x_2^g$. Consequently, *a vapour is relatively richer in the substance whose addition to a mixture increases the total vapour pressure or at a given pressure lowers the boiling point* **(Konovalov's first law).**

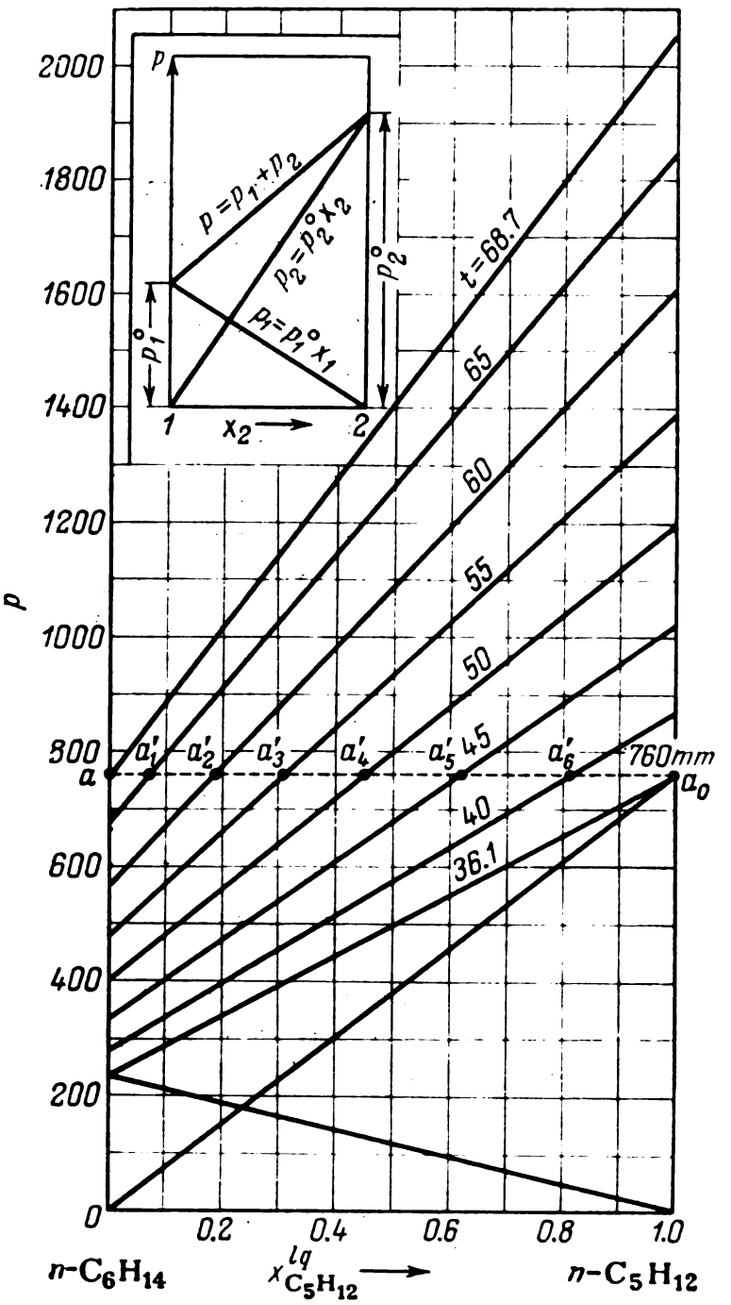

Fig. 96. Dependence of the partial and total vapour pressures on the composition of an ideal solution.

System hexane-pentane

If we know the dependence of the vapour pressure on the composition of a solution for several temperatures and the boiling points of the pure liquids, we can construct a diagram showing the dependence of the boiling point on the composition of a solution at a given pressure. Such a diagram is depicted in Fig. 98. It has been constructed from the data of Fig. 96.

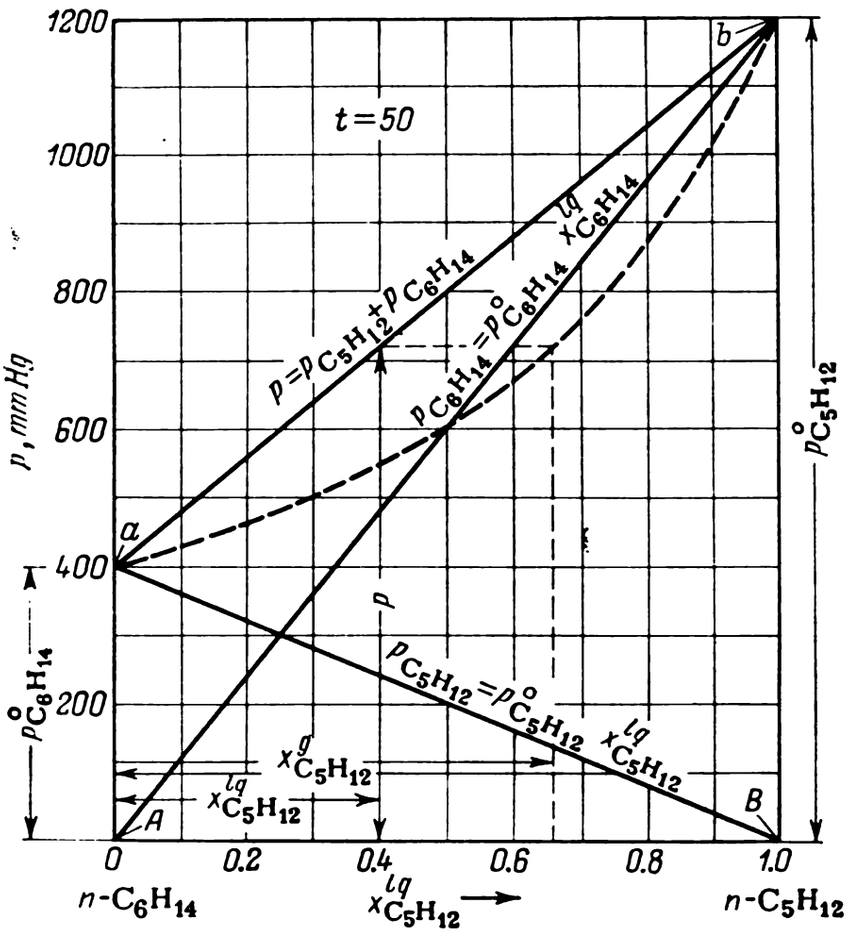

Fig. 97. Pressure-composition diagram for an ideal solution and a mixture of ideal gases.
The isotherm is in the system hexane-pentane

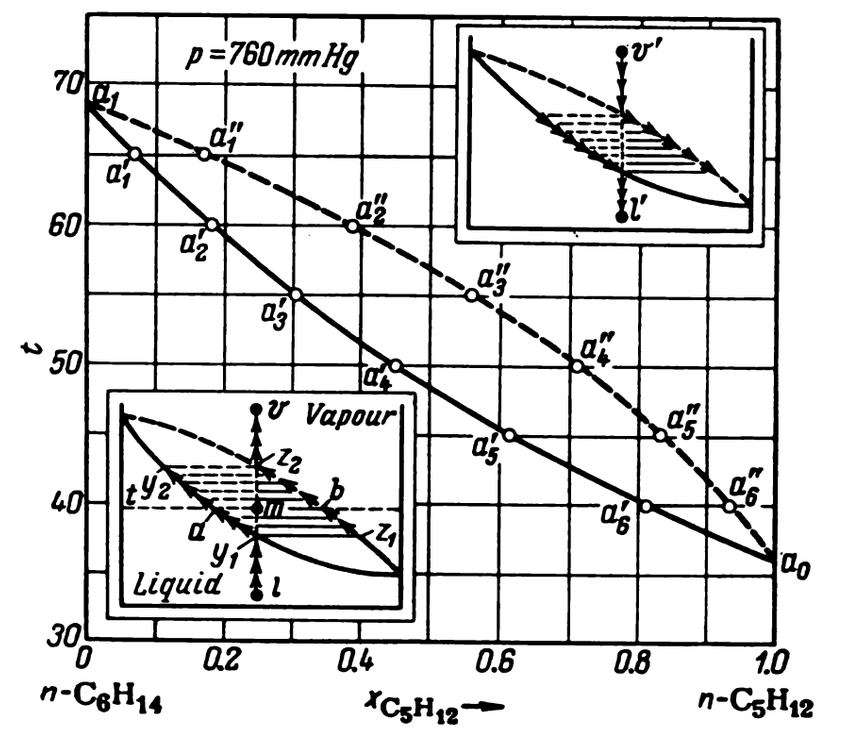

Fig. 98. Temperature-composition diagram.
The isobar in liquid-vapour equilibrium is for the system hexane-pentane

Curve $a_1a_1'a_2'\ldots a_0$ is a **boiling curve**; under it is the region of a non-boiling liquid. Curve $a_1a_1''a_2''\ldots a_0$ is a **condensation curve**; above it is the region of a superheated vapour. Between the two curves is a region of coexistence of a liquid and a vapour (moist vapour). The composition of equilibrium phases is determined by the intersection of a given isotherm with the boiling and condensation curves, while the ratio between these phases in the heterogeneous region is determined according to the lever rule. Thus, when liquid l is heated or vapour v is cooled to the temperature t, the initially homogeneous system transforms into a heterogeneous one (point m of the system) and decomposes into a liquid (phase point a) and a vapour (phase point b) in accordance with the ratio *

$$\frac{\text{amount of liquid}}{\text{amount of vapour}} = \frac{mb}{am}$$

The results of the calculations are also presented in the form of a diagram of liquid composition against vapour composition. Usually the content of the component having a high volatility is laid off on the coordinate axes. In this case, we get a curve connecting the corners of a square and deviating upward from its diagonal.** This deviation diminishes with a decreasing difference between the volatilities of the liquids. Coincidence with the diagonal is a rare exception (certain stereoisomers, a mixture of ethene chlorohydrin with propene chlorohydrin).

10.1.2. Non-Ideal Solution-Mixture of Ideal Gases

Systems in which the dependences of the partial and total pressures on the composition are expressed by straight lines are the limit which real solutions approach to a certain extent. It is therefore

* Proof of the lever rule: assume that 1 kg of a liquid having the composition x_2 decomposes when heated into g^{lq} kg of liquid having the composition x_2^{lq} (point a) and g^g kg of vapour having the composition x_2^g (point b). Hence

$$1x_2 = g^{lq}x_2^{lq} + g^g x_2^g = g^{lq}x_2^{lq} + (1 - g^{lq})\, x_2^g$$

whence

$$g^{lq} = \frac{x_2 - x_2^g}{x_2^{lq} - x_2^g} \quad \text{and} \quad 1 - g^{lq} = g^g = \frac{x_2^{lq} - x_2}{x_2^{lq} - x_2^g}$$

or

$$\frac{g^{lq}}{g^g} = \frac{x_2 - x_2^g}{x_2^{lq} - x_2}$$

If we represent the straight line x_2^{lq}-x_2^g (line ab) in the form of a lever of the first kind with its fulcrum at m, equilibrium will exist on the condition that the masses g^{lq} and g^g fastened to the ends of the lever comply with this proportion.

** An exception are systems with azeotropic mixtures, whose curves intersect the diagonal in the graph (see below).

convenient to classify real solutions and the graphs corresponding to them according to the nature of the deviation from a linear relationship.

If the deviations are observed toward smaller values, they are called **negative** deviations from Raoult's law (Fig. 99); if experimental data are higher than the values calculated by Eq. (8.45), we have **positive** deviations of the vapour pressure (Fig. 100).

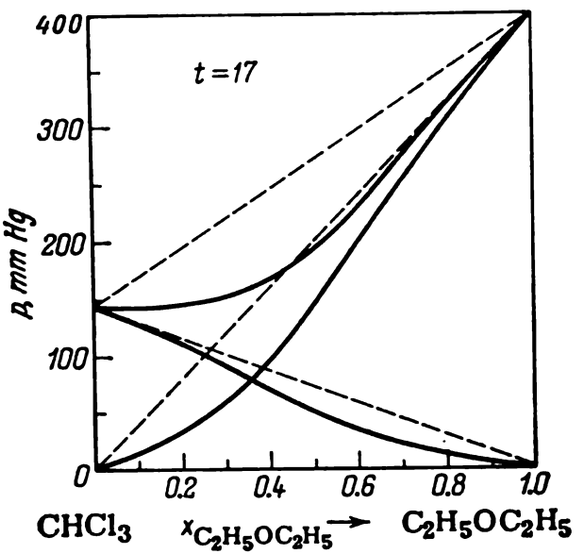

Fig. 99. Dependence of the partial and total vapour pressures on composition. A non-ideal solution (negative deviations from Raoult's law)

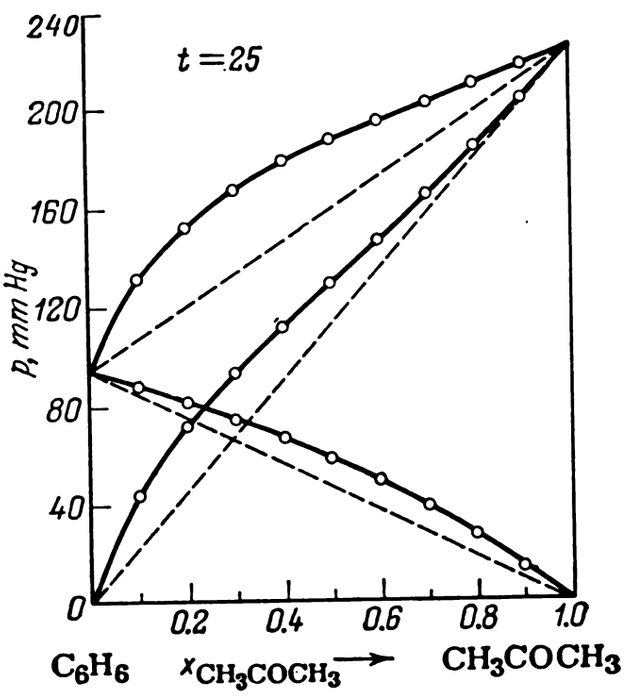

Fig. 100. Dependence of the partial and total vapour pressures on composition. A non-ideal solution (positive deviations from Raoult's law)

Systems of the first kind include solutions consisting of substances capable of reaction. Such solutions form with the liberation of heat (as a rule $\Delta V < 0$ for them). As a result, the heat of vaporization of a substance from a solution is greater than that of the pure substance. The lowering of the vapour pressure of a given substance caused by the dissolving of another substance is greater than the pressure increase that occurs. Hence, the total vapour pressure over the solution diminishes.

Systems of the second kind include solutions formed with the absorption of heat (as a rule $\Delta V > 0$ for them). Therefore, the heat of vaporization of a substance from a solution is less than that of thepure substance. Hence, the process of vaporization is facilitated, i.e. the vapour pressure grows (the increase in pressure predominates over the depression caused by solution).

Azeotropic Mixtures. An increase in the deviation from an ideal state may be attended by the appearance of a minimum with negative deviations (Fig. 101*a*) or a maximum with positive deviations (Fig. 101*b*). The greater the difference between the values of p_i°

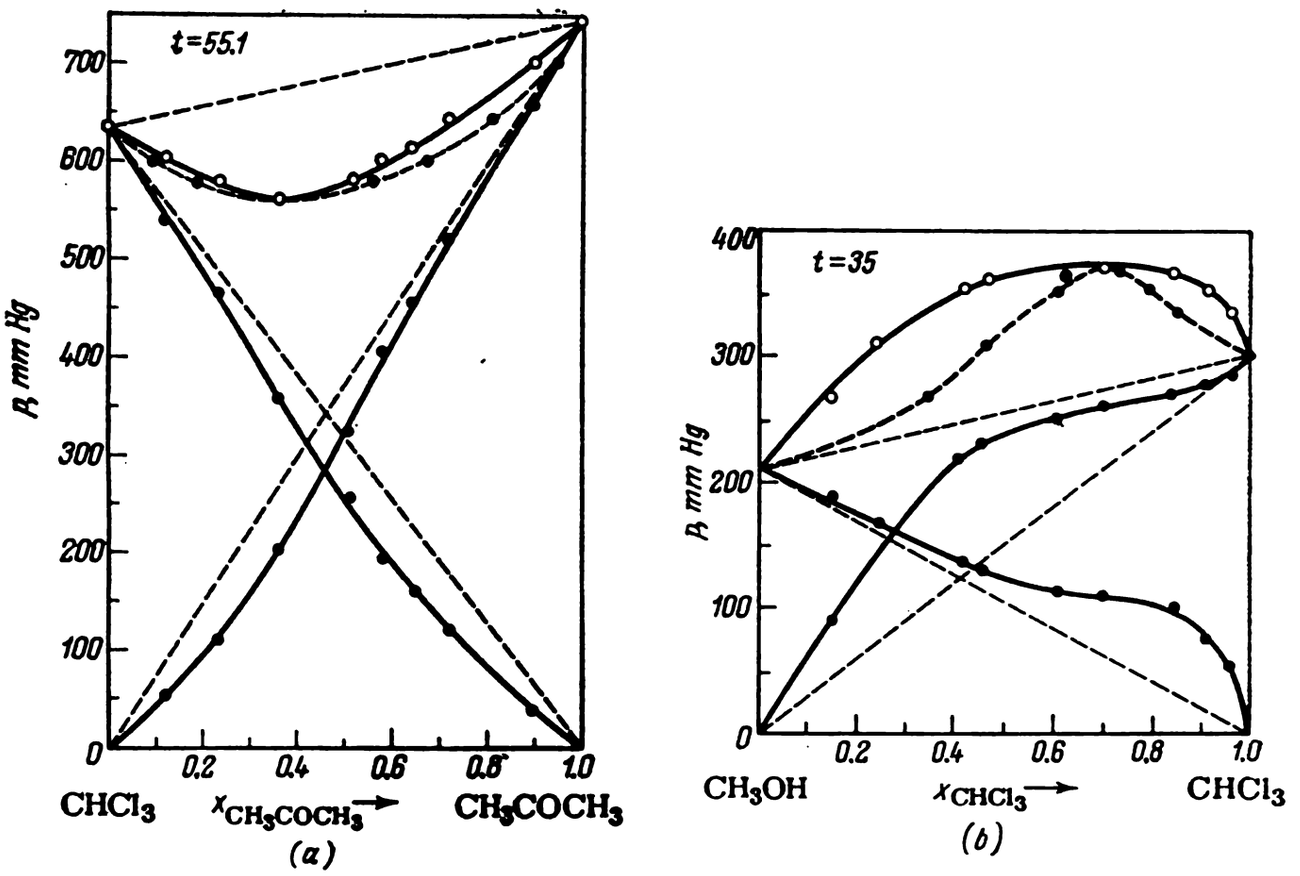

Fig. 101. Dependence of the partial and total vapour pressures on composition (non-ideal solution) :

a—negative deviations from Raoult's law with a vapour pressure minimum; *b*—positive deviations from Raoult's law with a vapour pressure maximum

and p_2° (or t_1° and t_2°), the greater must be the deviations for the formation of an extremum. In these cases, the vapour pressure of a whole series of mixtures having different compositions passes beyond the limits of the interval $p_1^\circ - p_2^\circ$. A minimum is typical of substances capable of dissociation, a maximum of substances capable of association.

A minimum on a pressure-composition diagram will obviously correspond to a maximum on a temperature-composition diagram, and, conversely, a minimum on the latter diagram will correspond to a maximum on the former.

The compositions of a liquid and a vapour coincide at points of an extremum of the vapour pressure (boiling points) (**Konovalov's second law,** *1881*).

Its validity can be proved by converse reasoning or as follows.

We shall delete the terms containing dx_2'' from Eq. (8.21). To do this, we multiply the first equation by x_1'' and the second by x_2''. After adding them and taking into account that $x_1'' x_2' - x_1' x_2'' = x_1''(1 - x_1') - x_1'(1 - x_1'') = x_1'' - x_1'$, we get

$$[(\bar{S}_1' - \bar{S}_1'')\, x_1'' + (\bar{S}_2' - \bar{S}_2'')\, x_2'']\, dT + [(\bar{V}_1'' - \bar{V}_1')x_1'' + (\bar{V}_2'' - \bar{V}_2')\, x_2'']\, dp + (x_2'' - x_1')\frac{\partial^2 G'}{\partial x_2'^2}\, dx_2'' = 0 \qquad (10.5)$$

Since at the points of an extremum $(\partial T/\partial x_2')_p = 0$ (on the boiling point-composition isobar) and $(\partial p/\partial x_2')_T = 0$ (on the pressure-composition isotherm), and the multipliers of dT and dp do not transform into infinity, while $\partial^2 G'/\partial x_2'^2 = 0$, then by dividing both parts of Eq. (10.5) by dx_2', we find that the extrema on the curves $p = \varphi(x_2')$ and $T = \varphi(x_2')$ correspond to the condition that $x_1'' = x_1'$ and $x_2'' = x_2'$.

After determining the values of $\partial^2 p/\partial x_2'^2$ and $\partial^2 T/\partial x_2'^2$, we can easily see that the second derivatives have opposite signs, i.e. a minimum on the curve $T = \varphi(x_2')$ corresponds to a maximum on the curve $p = \varphi(x_2')$ and vice versa.

Thus, the presence of extrema indicates that the composition of the phases is identical.

Mixtures for which the vapour in equilibrium with the liquid has the same composition in the given conditions as the liquid mixture are called **azeotropic** *. These mixtures are also called **constant boiling**, because upon distillation a condensate is formed having the same composition as the original mixture, and in these condi-

* From the Greek "zein" — to boil and "tropos" — turn ("a" is a negative prefix).

tions separation of a mixture is excluded. For the extremal points from Eq. (5.47) we have $f = 2 - 1 - 2 + 2 = 1$, while for $p = \text{const}$ (or $T = \text{const}$) we have $f_{\text{cond}} = 0$ (see p. 333).

Azeotropic mixtures (azeotropes) are mixtures with the greatest deviation from the ideal state that still have complete mutual solubility. A slight additional deviation from the ideal state results in the appearance of a region of mutual insolubility (see Sec. 10.3).

Figure 102 shows schematic diagrams of all the considered kinds of solutions in the coordinates pressure-composition (*a*), temperature-composition (*b*), and liquid composition-vapour composition (*c*). It summarizes the above material in a graphical form. It should be noted that the second and third diagrams for the first three kinds of solutions are identical.

For non-ideal solutions, Konovalov's first law holds as previously, although for azeotropes the addition of a more volatile component does not increase the vapour pressure over the solution for all compositions.

The appearance of an extremum is possible not only in systems whose components considerably differ in properties, but also in systems with substances having an almost identical vapour pressure (boiling points), when a slight deviation from a linear relationship results in the appearance of an extremum.* In such cases, the extremal point is in the middle of the diagram, whereas with a large difference between the values of p_1° and p_2° (or t_1° and t_2°) it is displaced toward the edge of the diagram — for a minimum vapour pressure toward the excess amount of the less volatile component, and for a maximum pressure toward the more volatile component. This displacement grows with an increasing difference between p_1° and p_2° (or t_1° and t_2°).

The coordinates of the extremal points (x_2^{lq}, p) can be found from the equation proposed by V. Kireev (1941):

$$\frac{1}{x_2^{\text{lq}}} = \sqrt{\frac{\ln p_2^\circ - \ln p}{\ln p_1^\circ - \ln p}} + 1 \qquad (10.6)$$

whose coincidence with experimental results is usually the better, the more symmetrical is the deviation of the relationship $p = \varphi(x_2^{\text{lq}})$ from linear and the smaller is the flatness of the extremum.

Generalizing Eqs. (8.21), A. Storonkin derived a group of laws called **Vrevsky's laws.**

---

* The vapour pressure for mixtures of optical antipodes for which $p_1^\circ = p_2^\circ$ does not depend on the composition and equals the vapour pressure over the pure components, i.e. the line $p = \varphi(x)$ is horizontal.

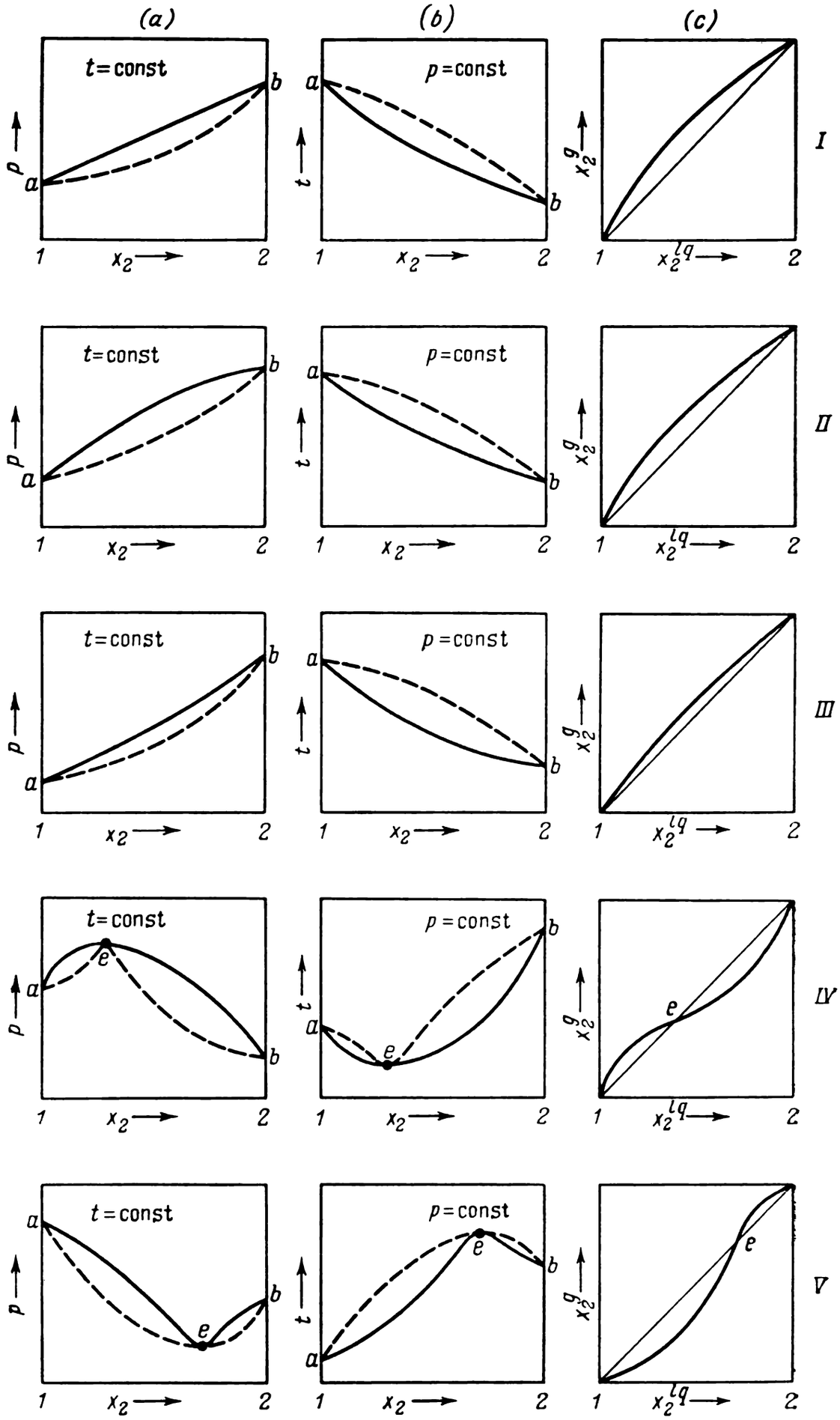

Fig. 102. Various kinds of liquid-gas equilibrium diagrams

Vrevsky's first law states that *when the temperature of a solution having a given composition is elevated, its vapour becomes richer in the component for which the differential heat of vaporization is greater.**

Vrevsky's second law determines the influence of a change in temperature and pressure on the composition of systems having a pressure or temperature extremum: *if the pressure (temperature) of a solution-vapour system has a maximum, then elevation of the temperature in an azeotropic mixture is attended by a growth in the concentration of the component whose differential heat of vaporization is greater; if the pressure (temperature) of a solution-vapour system has a minimum, then elevation of the temperature in an azeotropic mixture is attended by a growth in the concentration of the component whose differential heat of vaporization is smaller.* This law holds for states of binary systems far from critical.

Vrevsky's third law establishes the relationship between the displacements of the composition of a system having an extremum of pressure and temperature and the property of the phase that is stable above the temperature of coexistence when the pressure or temperature is changed: *a change in the temperature (pressure) of a solution whose saturated vapour pressure curve has a maximum is attended by a change in the composition of the solution vapour and in the composition of the azeotropic mixture in one direction. When the curve has a minimum, these compositions change in opposite directions.*

It follows that while Konovalov's laws describe the change in the state of systems for the condition $p = \text{const}$ or $T = \text{const}$ and establish the relationship between the changes in the pressure or temperature of coexistence of the phases and the changes in the composition of one of the phases in these conditions, Vrevsky's laws describe the change in the state of systems when restrictions are imposed on changes in their composition, either in the form of the condition that the composition of one of the coexisting phases be constant, or that the composition of the two coexisting phases be equal. Thus, Vrevsky's laws establish the relationship between a change in pressure or temperature and changes in the composition when the above restrictions have been imposed on the latter.

Figure 103 illustrates Vrevsky's second law. The experimental data shown correspond to the following values at $T_{\text{n.b.p.}}$: $\Delta H_{\text{vap}} = 1.79$ kcal/mol for HF and 6.58 kcal/mol for ClF_3, i.e. ΔH_{vap} for ClF_3 is greater than for HF.

The nature of the influence of pressure or temperature on the composition of an azeotropic mixture can be assessed according to

* Because of the absence of the relevant data, the heats of vaporization of the pure components are generally used instead of the partial molar heats of vaporization. The errors due to this substitution are the smaller, the bigger is the difference between the heats of vaporization of the components and the smaller are their heats of mixing.

the shape of the extremum. The sharper it is, the smaller is the change in the composition with a change in pressure or temperature. Conversely, with a flat extremum even a comparatively slight change in pressure or temperature leads to a significant change in the composition of an azeotropic mixture. The same relates to systems in which one component is greatly associated and the other is non-polar. In this case, the tendency to stratification becomes appreciable.

Research on azeotropic mixtures is of considerable practical interest. At present, the number of known binary azeotropic mixtures alone exceeds 3500. They include mixtures of H_2O and HNO_3, H_2O and HCl, H_2O and C_2H_5OH and others important in industry.

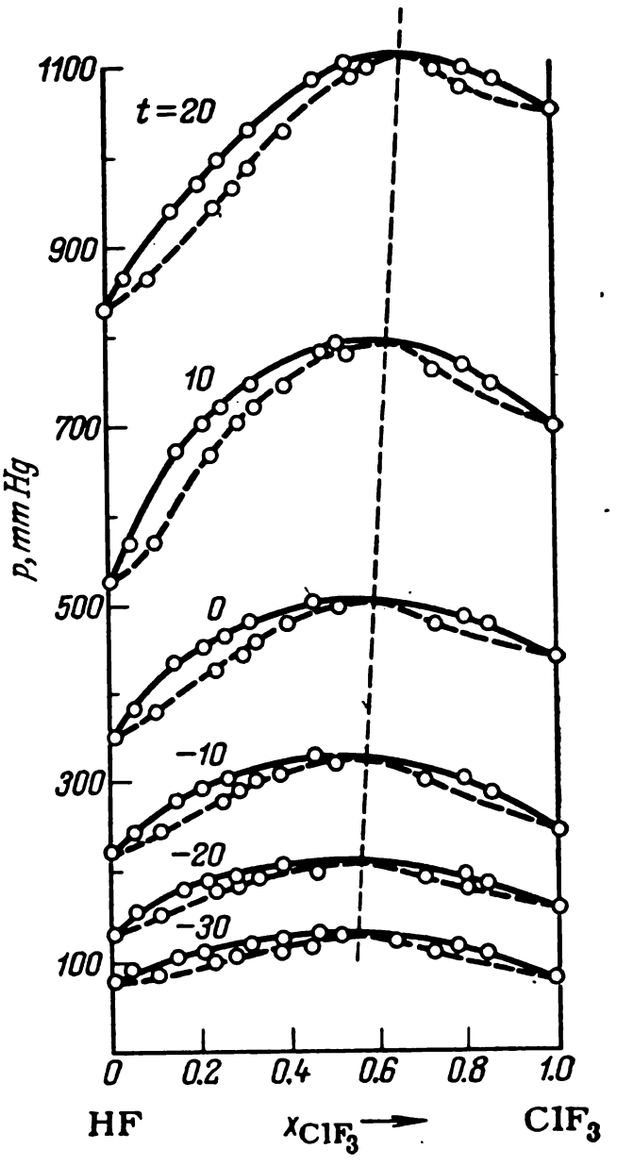

Fig. 103. Influence of temperature on the composition of an azeotropic mixture

Vapour Pressure. We shall turn to Eq. (8.17) for calculating the vapour pressure over a non-ideal solution. Writing it down for $\bar{Y} = \bar{G}$ and taking into account that at low pressures $f_i = p_i$, after cancelling out RT we get for a binary solution

$$x_1^{lq}\, d \ln p_1 + x_2^{lq}\, d \ln p_2 = 0 \quad \text{or}$$

$$\left(\frac{\partial \ln p_2}{\partial \ln p_1}\right)_T = \frac{\partial \ln x_2^{lq}}{\partial \ln x_1^{lq}} = -\frac{x_1^{lq}}{x_2^{lq}} \tag{10.7}$$

Equation (10.7) allows us to use the curve showing the dependence of the partial pressure of one of the components on the composition of a solution to plot a curve for the second component if at least one point on this curve is known for it. Calculations according to

Eq. (10.7) may lead to improper conclusions because of the inaccuracy of separate data (for instance the absence of agreement between p_1 and p_2) or because of the deviation of the system from Dalton's law (for example upon association in the vapour). This deviation can easily be taken into account by substituting the fugacities of the components for their partial pressures.

At $x_1^{lq} \to 1$, the vapour pressure of the components is determined by the equation $p_1 = p_1^\circ x_1^{lq}$ (8.45) and $p_2 = k_2 x_2^{lq}$ (8.51). At $x_2^{lq} \to 1$, the equations $p_2 = p_2^\circ x_2^{lq}$ (8.45) and $p_1 = k_1 x_1^{lq}$ (8.51) are used.

The following empirically found solution of Eq. (10.7) is generally used for calculations within the entire range of concentrations:

$$\left.\begin{aligned} p_1 &= p_1^\circ x_1^{lq} \exp\left[\frac{\alpha_2}{2}(1 - x_1^{lq})^2 + \frac{\alpha_3}{3}(1 - x_1^{lq})^3\right] \\ p_2 &= p_2^\circ x_2^{lq} \exp\left[\frac{\alpha_2 + \alpha_3}{2}(1 - x_2^{lq})^2 - \frac{\alpha_3}{3}(1 - x_2^{lq})^3\right] \end{aligned}\right\} \quad (10.8)$$

which can be considered sufficiently accurate.

If the values of p_1° and p_2° are known, the constants α_2 and α_3 can be computed either from the values of the partial pressures p_1 and p_2 for one composition (by solving two equations with two unknowns). or from the equations

$$\left.\begin{aligned} \frac{\alpha_2}{2} + \frac{\alpha_3}{3} &= \ln\left[\left(\frac{\partial p}{\partial x_1^{lq}}\right)_{x_1=0} + p_2^\circ\right] - \ln p_1^\circ \\ \frac{\alpha_2}{2} + \frac{\alpha_3}{6} &= \ln\left[p_1^\circ - \left(\frac{\partial p}{\partial x_1^{lq}}\right)_{x_1=1}\right] - \ln p_2^\circ \end{aligned}\right\} \quad (10.9)$$

on the basis of the values of the slopes of tangents to the curve $p = \varphi(x)$ at the points $x_1 = 0$ and $x_1 = 1$.

Both methods have their drawbacks. The first of them requires that the saturated vapour pressure be determined, which involves the use of complicated equipment and a time-consuming analysis of the vapour phase. The second requires graphical differentiation, which is not always sufficiently reliable at the point of termination of the curve.

N. Litvinov proposed the following method. The calculations are performed on the basis of two values of p (at $x_1^{lq} = 0.95$ and $x_1^{lq} = 0.05$).* If the properties of a mixture do not deviate very greatly

* If there is an extremum beyond the limits of $x_1^{lq} = 0.05$ to 0.95 on the vapour pressure curve, then Eqs. (10.10) and (10.11) given below must be replaced.

from those of ideal solutions, the constants of Eq. (10.8) can be found approximately by the equations *

$$\left.\begin{aligned}\frac{\alpha_3}{3} &= -\frac{4.606}{4x_1^3 - 3x_1^2}\log\frac{(px_1 - x_1p_1^\circ)p_1^\circ}{(px_1' - x_1p_2^\circ)p_2^\circ}\\ \frac{\alpha_2}{2} &= \frac{2.303}{x_1^2}\log\frac{px_1 - x_1p_2^\circ}{x_1'p_1^\circ} - x_1\frac{\alpha_3}{3}\end{aligned}\right\} \qquad (10.10)$$

where it is recommended to assume that $x_1^{lq} = 0.95$ and $x_1'^{lq} = 0.05$ (for more accurate results 0.99 and 0.01, respectively). If a mixture is far from ideal, the following equation should be used for calculations:

$$\begin{aligned}p = {} & \frac{0.9p_1^\circ - 0.9p_2^\circ - p_{x_1=0.95} + p_{x_1=0.05}}{0.042\,75}x_1^3 + \\ & + \frac{1.8p_2^\circ - 0.9p_1^\circ - 1.05p_{x_1=0.95} - 1.95p_{x_1=0.05}}{0.042\,75}x_1^2 + \\ & + \frac{0.042\,75p_1^\circ - 0.04275p_2^\circ - 0.05p_{x_1=0.95} + 0.95p_{x_1=0.05}}{0.042\,75}x_1 + p_2^\circ \qquad (10.11)\end{aligned}$$

from which the derivatives $(\partial p/\partial x_1^{lq})_{x_1^{lq}=0}$ and $(\partial p/\partial x_1^{lq})_{x_1^{lq}=1}$ are determined, and then the constants α_2 and α_3 are computed by Eq. (10.9). The values of these constants are used to calculate p_1 and p_2 by Eq. (10.8), and then $p = p_1 + p_2$ is determined.

Regardless of how the relationship between the pressure and the composition of a solution has been found, the composition of the vapour is determined by Dalton's law.

Liquid-vapour equilibrium can also be calculated by the equation

$$\frac{x_1^g}{x_2^g} = \alpha\frac{x_1^{lq}}{x_2^{lq}} \qquad (10.12)$$

where α is an empirical constant.

For ideal solutions, in accordance with Eq. (10.3), we have $\alpha = p_1^\circ/p_2^\circ$. With insignificant deviations from the ideal state $\alpha \approx$ const (both for isobars and isotherms). Equation (10.12) is convenient for processing experimental data if we express the constant α as an approximate function of pressure.

The Kireev-Othmer method can also be used to establish the relationship $p_x = \varphi(T)$ (see Sec. 7.2.3).

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* The superscript "lq" has been omitted in Eqs. (10.10) and (10.11) for simplification.

10.1.3. Separation of Solution Components

Single Evaporation. The process of **single evaporation or distillation in equilibrium (single condensation)** is conducted at a constant total composition. If a liquid mixture (point l in Fig. 98, p. 321) is subjected to isobaric heating, then after the boiling point is reached (point z_1) and heat equal to δQ is supplied, the first bubble of vapour will appear (having the composition y_1) that is richer in the easily volatile component than the original liquid. As a result, the liquid becomes richer in the high-boiling component, which increases its content in the following portions of vapour and elevates the boiling point (the initial point will move upward along the boiling curve). Since the process occurs without the removal of the vapour, the ratio of the amount of vapour to that of liquid continuously grows.

If the supply of heat continued to complete evaporation of the liquid, the vapour formed from the last droplet of the liquid would have a composition (point y_2) coinciding with that of the initial liquid, while the microscopic residue of the liquid passing into the vapour phase would have the composition z_2. [The process of single condensation is also schematically shown in Fig. 98 (v'-l').] The arms of the levers corresponding to the liquid phases are shown by solid lines, and those corresponding to the vapour phases by dashed lines. The diagrams show how the composition of the phases and the ratio between them change with temperature (the lever rule).

Separation of the components of a solution by single evaporation or distillation in equilibrium is simple and especially convenient when the boiling points of the pure substances sharply differ or when it is only necessary to enrich a mixture with one of its components. In practice, only a part of the liquid is usually evaporated. Thus, if the vapour formed is condensed when the temperature t is reached (see Fig. 98), then about 40% (of the original amount) of a mixture having composition b will be obtained.

Simple Distillation. Distillation in equilibrium with the liquid, when the vapour formed is removed and condensed, is called **differential** or **simple distillation (gradual evaporation).**

The ratio between the weight and composition of the distillate and the residue will be different in single and in gradual evaporation.

Rectification. Neither differential distillation nor single evaporation can ensure complete separation of a mixture. True, in the former case an almost pure component can be obtained, but its amount will be insignificant. Fine separation is achieved by **rectification**, a combination of sequential evaporations and conden-

sations (Fig. 104). This process is conducted in rectification columns whose operation is schematically shown in the same figure. Rectification is based on the following principle: if a liquid having the composition L and a vapour having the composition V supplied to a given plate are not in equilibrium, then heat and mass exchange occurs between them. These processes will result in (1) displacement of the composition of the vapour and of that of the liquid in the directions indicated by the arrows; and (2) cooling of the vapour resulting in its partial condensation (point P') and heating of the liquid resulting in its partial evaporation (point P''). Thus, the ascending vapour, losing its high-boiling component because of contact with the liquid and acquiring the low-boiling component, becomes enriched with the latter. The liquid, flowing downward along overflow pipes as it accumulates on the plates, is gradually enriched with the high-boiling component. With a sufficient quantity of plates, their number being calculated for a definite completeness of separation, it is possible to obtain a vapour with a minimum content of the high-boiling component. When a mixture of a definite composition is needed, the vapour (liquid) is tapped from a definite height of the column.

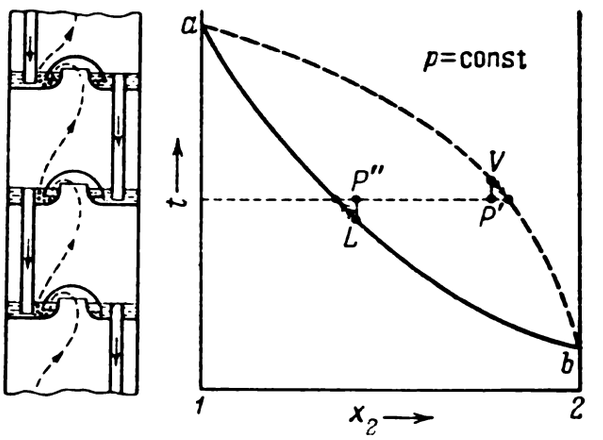

Fig. 104. Schematic view of a rectification column and diagram showing its operating principle

In packed columns, the compositions of the liquid and vapour change continuously.

The difference between the properties of the phases becomes more and more insignificant toward the bottom and top of the column (points a and b), and absolutely complete separation of the liquid subjected to rectification is impossible. This would obviously require an infinitely great number of plates or a correspondingly infinitely great height of the packing.

If a temperature-composition or pressure-composition curve has a maximum or a minimum, then regardless of the initial composition of the liquid, the latter is not distilled completely. Only a pure component and a constant-boiling (azeotropic) mixture can be obtained. The stopping of rectification (or simple distillation) at the extremal points is explained by the composition of the liquid coinciding with that of the vapour, causing the driving force of distillation — the difference between the composition of the phases — to equal zero. Therefore, in equilibrium, an azeotropic

mixture evaporates like a pure substance. In this sense, we can assume Fig. 102, *IV* and *V* to consist of two diagrams similar to Fig. 102, *I-III*: "component 1-azeotropic mixture" and "azeotropic mixture-component 2".

Apart from a change in pressure and temperature, the introduction of a third substance is used to separate azeotropic mixtures. Here the chemical nature of the components comes to the forefront, because the addition of a third substance causes a different change in the vapour pressure of the mixture components.

The high theoretical effectiveness of the rectification process (complete separation, large yields, a favourable heat balance) is not reached in practice because of the many irreversible phenomena. A number of simplifying assumptions are usually made in calculations (equilibrium between the liquid and vapour at each level, a homogeneous composition of the liquid on each plate, the minimum work is needed for separation, the liquid is an ideal solution, etc.).

To determine the actual number of plates, we must take into account the properties of the components, the duration of contact between the liquid and vapour, the depth of the layer of liquid on a plate, the spacing of the plates and their design, the pressure drop along the height of the column due to flowing of the liquid, the heat losses through the column walls, etc. It is not difficult to foresee deviations from ideal conditions, but their precise quantitative calculation is impossible; therefore the values of the efficiencies of rectification columns can be only approximately correct.

10.2. LIQUID-GAS EQUILIBRIUM FOR COMPLETELY MISCIBLE LIQUIDS AT HIGH PRESSURES

At a high pressure, the components of a mixture do not obey Eq. (8.45). At the same time, the vapour phase cannot be considered as a mixture of ideal gases, i.e. Eq. (6.14) cannot be used. Therefore, calculation of equilibrium by Eq. (10.2) leads to great errors.

The following equation is used instead of Eq. (10.2):

$$f_i = (f_i^{lq})_p^\circ \; x_i^{lq} = (f_i^g)_p^\circ \, x_i^g \text{ or } \frac{x_i^g}{x_i^{lq}} = \frac{(f_i^{lq})_p^\circ}{(f_i^g)_p^\circ} = K_i = \varphi(p, T) \quad (10.13)$$

whence

$$x_1^{lq} = \frac{1 - K_2}{K_1 - K_2} \text{ and } x_2^{lq} = \frac{1 - K_1}{K_2 - K_1} \quad (10.14)$$

In Eq. (10.13), the fugacities of the pure component in the liquid and gaseous phases are taken at the temperature and pressure of the solution (Fig. 105). For a moderate pressure, the fugacity of a pure liquid component under the total pressure may be replaced with its fugacity at the saturated vapour pressure (at the given temperature). When the difference between p and p_i° is considerable, the calculations must be repeated by Eq. (8.41) :

$$\ln \frac{(f_i^\circ)_p}{(f_i^\circ)_{p_i^\circ}} = \frac{1}{RT} \int_{p_i^\circ}^{p} V_i^\circ \, dp$$

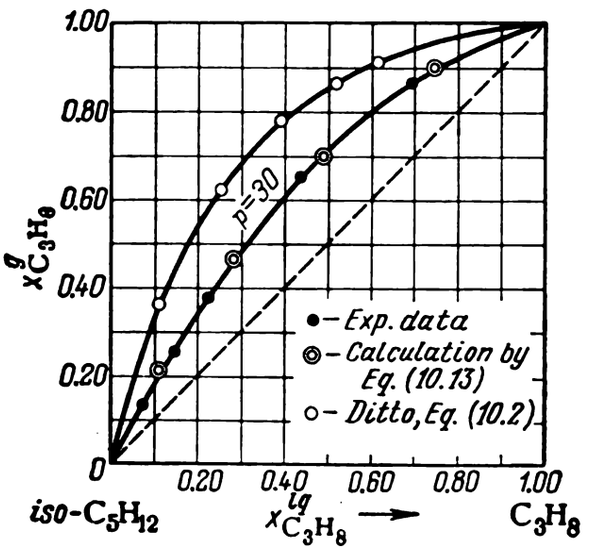

Fig. 105. Equilibrium compositions of liquid and vapour at high pressures in the system propane-isopentane. Checking of Eqs (10.2) and (10.13). (See Example 4)

Equation (10.13), like Eq. (10.2), can naturally be applied only to ideal solutions. In other words, Eq. (10.13) does not allow us to find the composition of a vapour (liquid) with a high accuracy when the deviation from the additivity of volumes is considerable. For non-ideal solutions, K_i will depend not only on the temperature and pressure, but also on the concentration, and for any component $K = 1$ at the critical point of the mixture (see below) and at the vapour pressure of the pure component (at a given temperature).

Liquid-gas equilibrium is most often calculated according to the partition coefficients. The latter are generally used in the form of graphs of $K = \varphi(p, T)$ in recurring calculations for concrete systems. The nomogram in Fig. 106 combines data for a number of hydrocarbons.

To determine the composition of one of the phases (for example the vapour), the known composition of the other phase is used to calculate π and τ and determine the fugacity of the pure substances in the liquid state at a pressure equal to the saturated vapour pressure at the temperature of the system. If the pressure in the system differs considerably from this pressure, Eq. (8.41) is used to make the calculations more accurate. Next the fugacities of the pure components in the gaseous phase are calculated for the temperature and total pressure of the system. Finally, the composition of the vapour is determined by Eq. (10.13). If the assumed pressure is sufficiently close to the actual value, the sum of the mole fractions of the components in the gaseous phase should equal unity. If $\Sigma x_i^g \neq 1$, assuming a different vapour

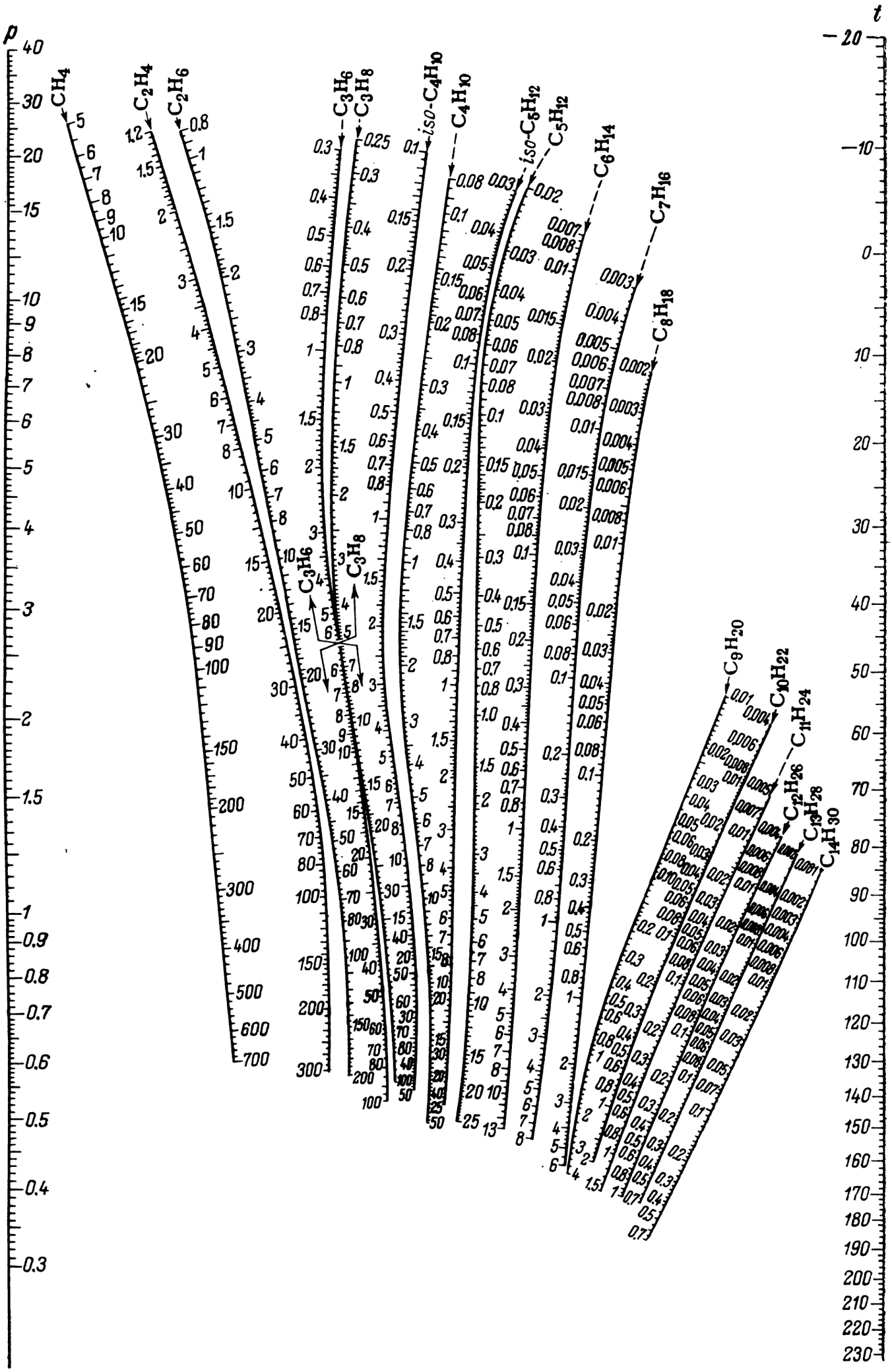

Fig. 106 . Dependence of partition coefficients of selected hydrocarbons on temperature and pressure

pressure, we repeat the calculations until the discrepancy is within the value of the experimental error. In practice, these calculations have to be performed not more than three or four times.

It is often necessary to calculate the phase equilibrium of hydrocarbons within a very broad interval of temperatures and pressures. Special graphs have been constructed for these calculations. They include the regions in which the pressures are higher and the temperatures are lower than the critical ones, i.e. the liquid is the stable phase. In this region, the fugacity can be found only with the aid of experimental data on the distribution of the components in the liquid and gaseous phases. A graph of this kind is shown in Fig. 107. The lines $\tau = \text{const}$ in this region are separated from the zone of stability of the gaseous phase by curve ABC. Below it, the graph has been constructed according to experimental values of the partition coefficients, and the ratio $(f_i^{lq})^\circ_{p,T}/(f_i^g)^\circ_{p,T}$ has been replaced by the ratio $(f_i^{lq})^\circ_{p_i^\circ}/(f_i^g)^\circ_{cond}$, where $(f_i^g)^\circ_{cond}$ is selected so that when the fugacity of a liquid under the total pressure is replaced with its fugacity at the saturated vapour pressure, the ratio (10.13) will not change. Therefore, Fig. 107 is especially convenient when it is necessary to determine the fugacity of a liquid at such high pressures at which it is necessary to take into account the change in $(f_i^{lq})^\circ_p$ with the pressure, because the need to use Eq. (8.41) vanishes.

Figure 108 shows a graph for the direct determination of the fugacity of liquid hydrocarbons for the condition of their equilib-

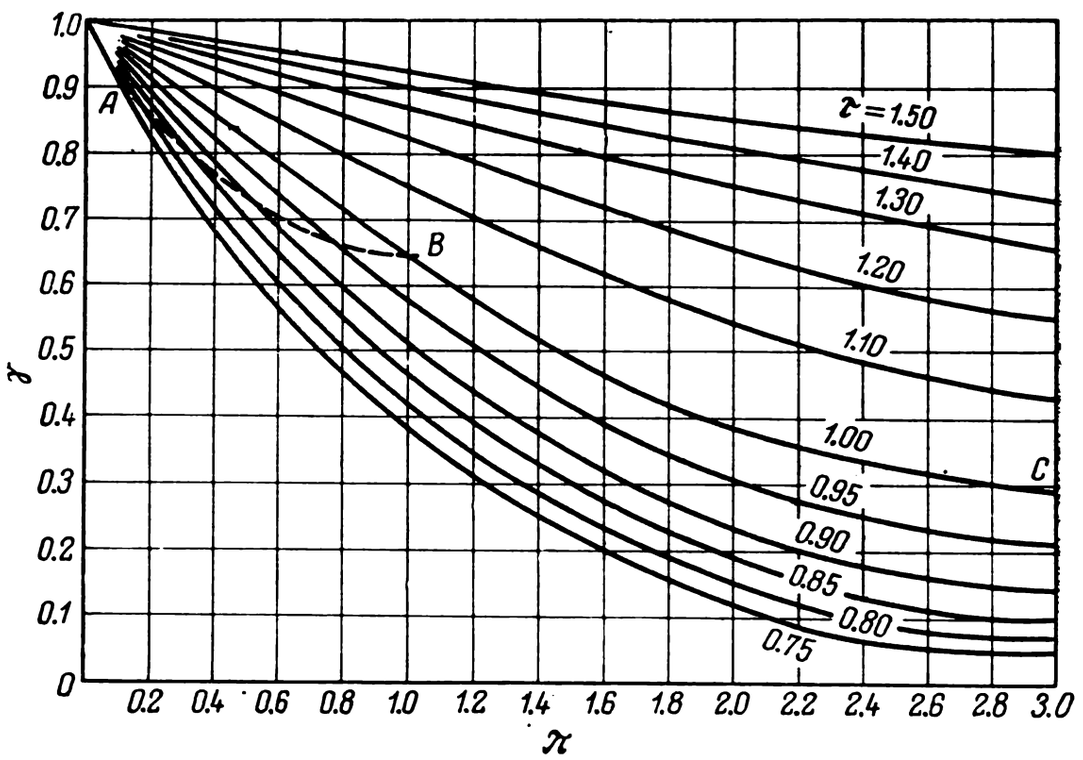

Fig. 107. Dependence of the activity coefficients of gaseous hydrocarbons on the reduced temperature and pressure [C9]

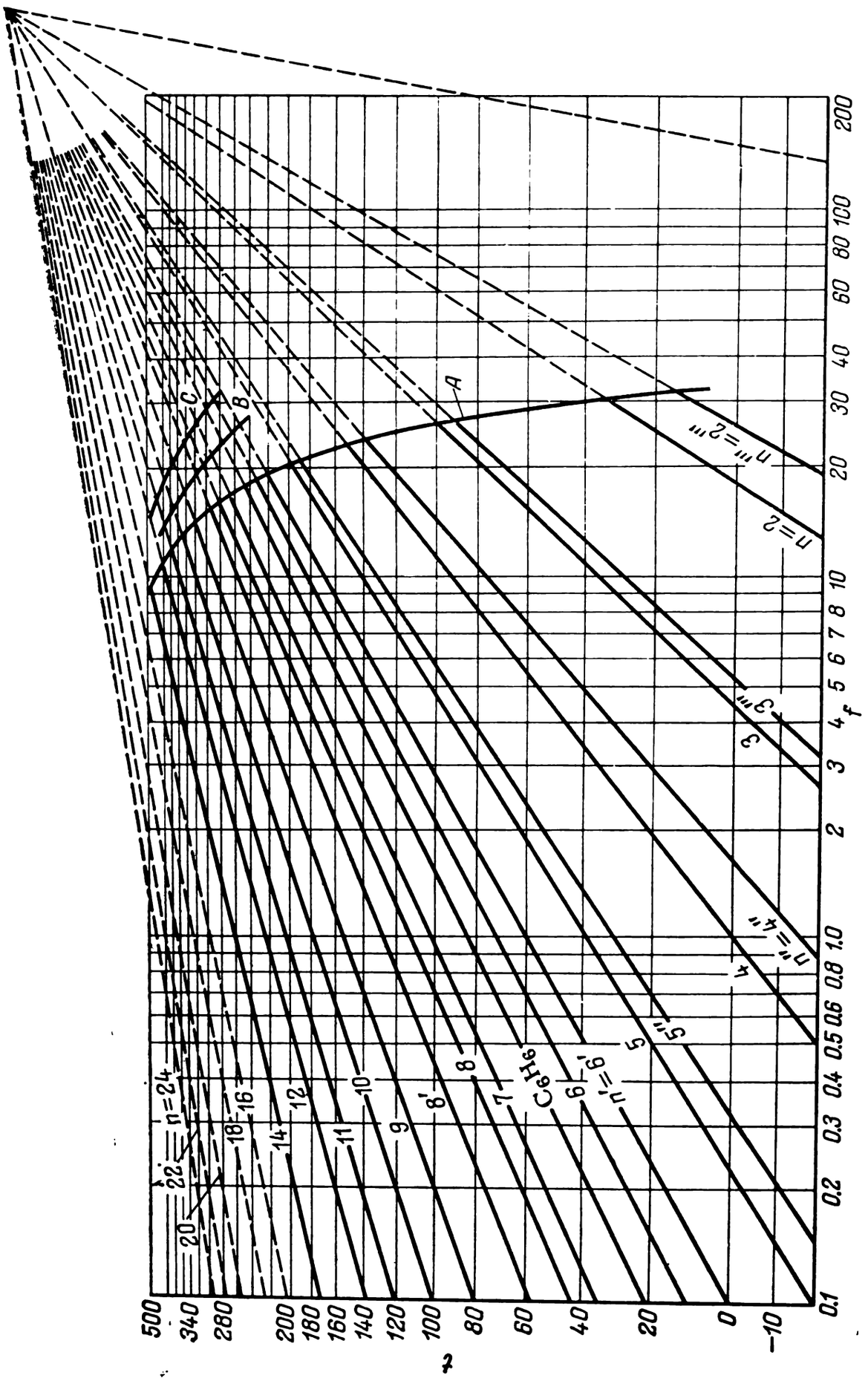

Fig. 108. Fugacities of liquid hydrocarbons [C9]:

n—alkanes; *n'*—diisoalkanes; *n''*—isoalkanes; *n'''*—alkenes. The numbers on the lines signify the number of carbon atoms in a molecule. Curves *A*, *B* and *C* combine the critical points of alkanes, naphthenes and aromatic compounds, respectively

rium with the vapour. This graph simplifies the calculations to an even greater extent, because it is no longer necessary to determine the value of the vapour pressure and extrapolate it above the critical temperature (if $T > T_{cr}$).

Example 1. Find the partition coefficient for propane (C_3H_8) at $t = 75$ °C and a total pressure of $p = 10$ atm.

Solution. Using the data given in Appendix 9, we calculate $\tau = 0.94$ and $\pi = 0.24$. Further from Fig. 40 (p. 192) we find $\gamma = 0.9$, whence the fugacity of pure gaseous propane at $t = 75$ °C and $p = 10$ atm equals $(f^g_{prop})^\circ = 9$ atm. The saturated vapour pressure of propane at 75 °C is $p^\circ_{prop} = 29$ atm (see Fig. 56) which corresponds to $\pi = 0.67$ ($\tau = 0.94$). From Fig. 40 we have $\gamma = 0.71$, which corresponds to the fugacity of the pure vapour and thus of the liquid propane in equilibrium with it $(f^{lq}_{prop})^\circ = 28 \times 0.71 = 19.9$ (at p°_{prop}). Considering that V^{lq} is constant, we recalculate the latter quantity into the fugacity of C_3H_8(lq) in actual conditions. For this purpose, we use Eq. (8.41), which in the given case becomes

$$\log \frac{f_p}{19.9} = \frac{112.5(10 - 28)}{2.303 \times 82.06 \times 348.2} = -0.0308$$

where $V^{lq}_{prop} = 112.5$ cm³ ($\rho = 0.391$ g/cm³) has been determined by Fig. 61 (p. 225). The calculations give $f_{p_{tot}} = 18.6$ atm. Notwithstanding the almost three-fold difference between the vapour pressure of the propane and the total pressure over the solution, $(f^{lq}_{prop})^\circ$ at p°_{prop} differs from $f_{p_{tot}}$ by only 7%.

From Eq. (10.13), we get $K = 18.6/9 \approx 2.1$. This result means that for any ideal solution the concentration of the propane in the gaseous phase will be 2.1 times greater than in the liquid. For a solution of C_3H_8 in *iso*-C_5H_{12}, experimental data give $K \approx$ ≈ 2.3 (see Figs. 106 and 114).

Example 2. Using the data in Fig. 107, calculate the fugacity of propane at $t = 30$ °C and $p = 20$ atm.

Solution. According to the values of $\tau = 0.82$ and $\pi = 0.48$, we find from Fig. 107 that $\gamma = 0.68$ and $f = 13.6$ atm.

The vapour pressure of propane according to Fig. 56 at $t =$ $= 30$ °C is 11 atm, i.e. $\pi = 0.26$, while from Fig. 40 we have $\gamma = 0.85$ and $(f^g_{prop})^\circ = 0.85 \times 11 = 9.3$ (at p°_{prop}). Consequently, $0.68 = 9.3/f$, i.e. $f = 13.7$ atm.

Example 3. Calculate the partition coefficients of propane (C_3H_8) and isopentane (*iso*-C_5H_{12}) and the composition of the equilibrium phases at $p = 30$ atm and $t = 125$ °C using the data given in Figs. 107 and 108.

Solution. According to the values of the critical parameters (see Appendix 9), we calculate $\pi_{prop} = 0.71$, $\tau_{prop} = 1.08$, $\pi_{iso} = 0.91$ and $\tau_{iso} = 0.86$. From Fig. 107 we find $(f^g/p)_{prop} = 0.81$ and $f^g_{prop} = 24.3$ atm, $(f^g/p)_{iso} = 0.51$ and $f^g_{iso} = 15.3$ atm. From Fig. 108 we have $f^{lq}_{prop} = 36.5$ atm and $f^{lq}_{iso} = 9.2$ atm. Thus

$$K_{prop} = \frac{36.5}{24.3} = 1.5 \quad \text{and} \quad K_{iso} = \frac{9.3}{15.3} = 0.6$$

By Eq. (10.14) we calculate

$$x^{lq}_{prop} = \frac{1 - 0.6}{1.5 - 0.6} = 0.445 \quad \text{and} \quad x^g_{prop} = 1.5 \times 0.445 = 0.667$$

Consequently, the liquid consists of 44.5% of C_3H_8 and 55.5% of *iso*-C_5H_{12}, whereas the vapour consists of 66.7% of C_3H_8 and 33.3% of *iso*-C_5H_{12}. The results of the calculations agree well with the experimental data given in Figs. 105, 109, 113 and 114.

Example 4. On the basis of the data given in Fig. 113 for $p = 30$ atm, (1) construct a diagram of $x^g = \varphi(x^{lq})$ for C_3H_8 and (2) calculate phase equilibrium by Eqs. (10.13) and (10.2) for $t = 100$, 120, 140 and 160 °C. Compare the results of the calculations with experimental data.

Solution. After constructing a diagram of $x^g = \varphi(x^{lq})$ for propane (see Fig. 105), we consecutively calculate the partition coefficients and by Eq. (10.13) the composition (see Example 1). Next we find p°_{prop} (by extrapolation) and p°_{iso} (for isopentane) and calculate the values of x^{lq} and x^g for propane by Eq. (10.2). The results of this calculation are tabulated below.

t	Experimental data		K_{prop}	K_{iso}	By Eq. (10.13)		p°_{prop}	p°_{iso}	By Eq. (10.2)	
	x^{lq}_{prop}	x^g_{prop}			x^{lq}_{prop}	x^g_{prop}			x^{lq}_{prop}	x^g_{prop}
100	0.69	0.87	1.20	0.40	0.75	0.90	44	7.05	0.62	0.91
120	0.48	0.70	1.46	0.58	0.48	0.70	60	10.5	0.39	0.78
140	0.31	0.49	1.66	0.74	0.28	0.47	75	15.0	0.25	0.63
160	0.14	0.25	1.88	0.89	0.11	0.21	100	21.5	0.11	0.37

These results (see also Fig. 105) show that for the given conditions Eq. (10.13) gives good coincidence with the experimental data, whereas Eq. (10.2), even if we take into account the unreliability in extrapolating the temperature dependence of the vapour pressure of propane, yields unsatisfactory results.

Example 5. A mixture consisting of 47% of C_3H_8, 8% of *iso*-C_4H_{10}, 32% of *n*-C_4H_{10}, 4% of *iso*-C_5H_{12} and 9% of *n*-C_5H_{12} is liquefied.

Calculate the composition of the liquid phase and the pressure needed for condensation if $t = 93\,°C$.

Solution. Assigning an arbitrary value to the total pressure, we calculate K_i according to the nomogram (see Fig. 106), and then the composition of the liquid phase by Eq. (10.13). We repeat the calculations until the value of p_{tot} used complies with the condition $\Sigma x_i^{lq} = 1$. The results of these calculations are tabulated below. They show that condensation begins at a pressure somewhat higher than 17 atm.

Components	x_i^g	$p_{tot} = 15$		$p_{tot} = 17.5$		$p_{tot} = 17$	
		K_i	x_i^{lq}	K_i	x_i^{lq}	K_i	x_i^{lq}
Propane	0.47	2.10	0.235	1.90	0.247	1.95	0.241
Isobutane	0.08	1.15	0.070	1.04	0.077	1.06	0.075
Butane	0.32	0.94	0.341	0.85	0.377	0.87	0.368
Isopentane	0.04	0.50	0.080	0.46	0.087	0.47	0.085
Pentane	0.09	0.43	0.209	0.388	0.232	0.395	0.228
Total			0.925		1.020		0.997

10.2.1. Critical Phenomena

Equilibrium for pure substances at the critical point exists at p_{max} and t_{max}, and the properties of the phases are identical (see Sec. 7.3). Inspection of Fig. 109 shows that this is not observed for binary systems (also compare Fig. 61 on p. 225 with the drawing in the bottom right-hand corner of Fig. 109). The liquid phase may also exist in binary systems at $T > T_{cr}$ and $p > p_{cr}$, and the saturated vapour pressure may diminish with a growth in temperature (section p_{max}-C). Konovalov's first law and Vrevsky's laws cannot be applied to the critical region.

For a binary system having a given composition, there is a definite region of p and T in which upon isothermal compression of the vapour, partial condensation is followed by transformation of the liquid into the vapour. This transformation is called **reverse (retrograde) condensation.** The phenomenon of **reverse (retrograde) evaporation** is also possible: upon isobaric heating the liquid partly evaporates, but beginning from a definite temperature (different for different pressures) further heating results in a diminished amount of vapour; next the system again becomes homogeneous and completely transforms into a liquid.

This can be illustrated graphically. Curve yCz in Fig. 109 corresponding to a mixture of 60.7% of isopentane and 39.3% of propane includes a region containing two phases: to the right, downward from branch zC — the vapour, and to the left, upward from branch yC—the liquid. Condensation curve zC and boiling curve yC converge at **critical point** C, at which the difference between the properties of the two phases vanishes. Reverse condensation and reverse evaporation occur only when the heterogeneous region is intersected in the shaded portion (the shaded portion above the level of critical point C has been enlarged for convenience). Consequently, if entering and leaving the region confined by curve yCz are connected with intersection of the same curve, either Cz or Cy (processes ab and de), reverse condensation (evaporation) occurs. If a process takes place at a pressure and temperature below critical, i.e. corresponding to point C (processes fg and hl), then ordinary condensation (evaporation) occurs.

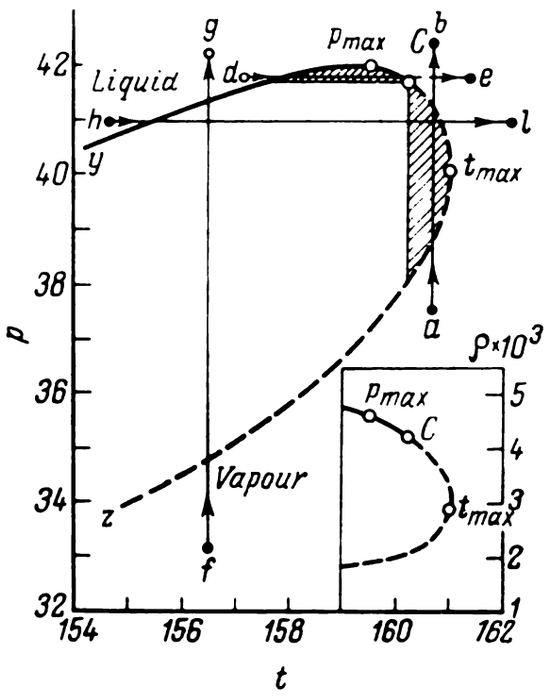

Fig. 109. A fragment of a pressure-temperature phase diagram with a constant composition in the critical region. System propane-isopentane ($x_{prop} = 0.393$)

Every composition has its own orthobaric loop of the shape yCz whose width and position change with the composition. The location of the critical point also changes: for mixtures rich in one of the components, it is to the right of p_{max} or below t_{max}; for other mixtures, it may shift to the left, passing through a maximum for a certain composition. As we pass over to systems in which one of the components predominates, this loop, being displaced in the system of coordinates p-T, narrows in accordance with the reduction in the difference between the composition of the liquid and vapour phases. Therefore, points p_{max} and t_{max} approach each other, and in the limit, when the composition corresponds to a pure substance, all three points (p_{max}, t_{max} and C) merge into one. The loop transforms into a curve of $p = \varphi(T)$ for the pure substance. Figure 110, constructed on the basis of data on phase equilibria in the system C_3H_8-*iso*-C_5H_{12}, illustrates the above.

Critical curve $C_{C_3H_8}$-C'-C''-...-$C_{iso\text{-}C_5H_{12}}$ **(the convolution point curve)** combines the critical points for mixtures of all compositions beginning with pure propane (point $C_{C_3H_8}$) and ending with pure

isopentane ($C_{iso\text{-}C_5H_{12}}$). The loops correspond to five different mixture compositions (curve yCz in Fig. 109 is an enlarged view of the upper part of the equilibrium curve for $x^{liq}_{iso\text{-}C_5H_{12}} = 0.607$).

Let us construct a three-dimensional temperature-pressure-composition diagram using the data of Fig. 110. This diagram (Fig. 111) gives a general picture of phase equilibrium. The temperature (boil-

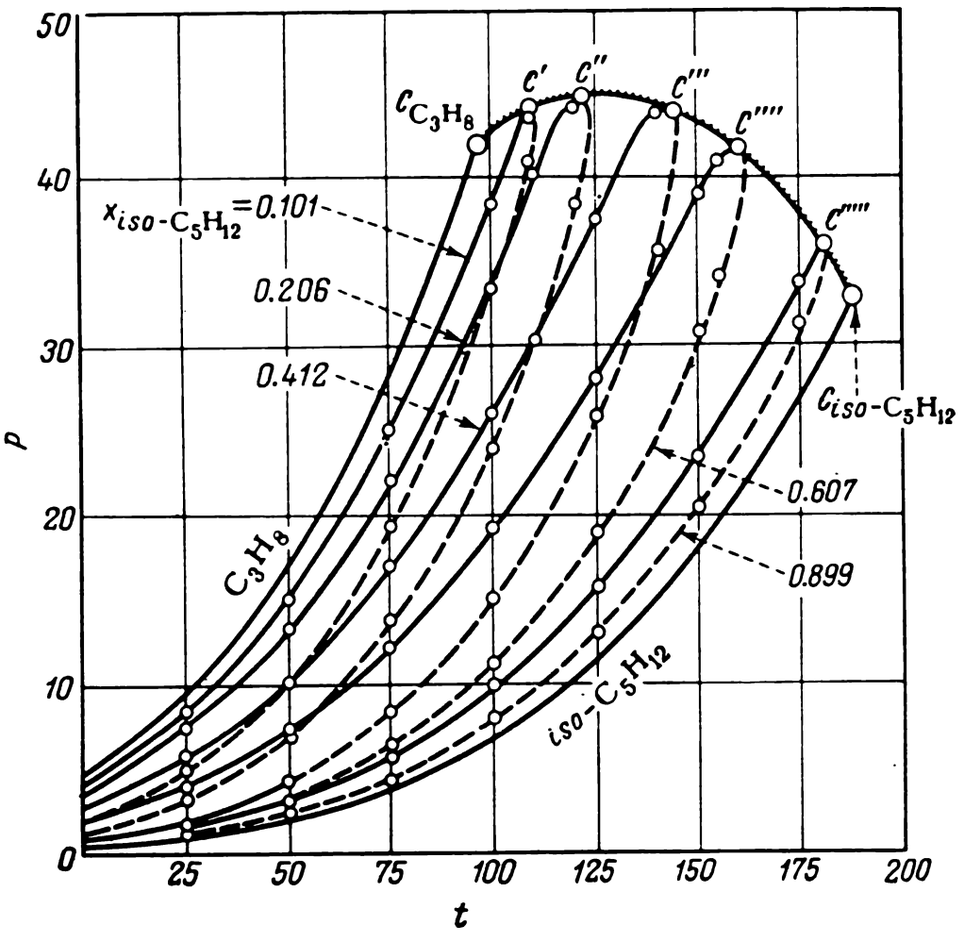

Fig. 110. Liquid-vapour equilibrium in the system propane-isopentane for mixtures of various compositions (*iso*-concentrates)

ing point) is laid off along the axis of abscissas, the pressure (vapour) along the axis of ordinates, and the mole fraction of *iso*-C_5H_{12} (x_2) in a direction at right angles to plane p-T. The curve $p^\circ_{C_3H_8} = \varphi(t)$ terminating at the critical point of propane (point C_1) is shown on the front plane of the coordinate parallelepiped (the plane of pure propane), and a curve showing the temperature dependence of the saturated vapour pressure of isopentane terminating at its critical point (point C_2) is shown on the rear plane. The two critical points are connected by a convolution point curve running from the front to the rear plane. This curve combines the critical points for binary systems of all compositions, including those whose equilibrium was studied in the given system (see Fig. 110). Five sections indicated in Fig. 111 by horizontal hatching correspond to them. The projections of the curve $p^\circ_{C_3H_8} = \varphi(t)$ and of the five sections by constant

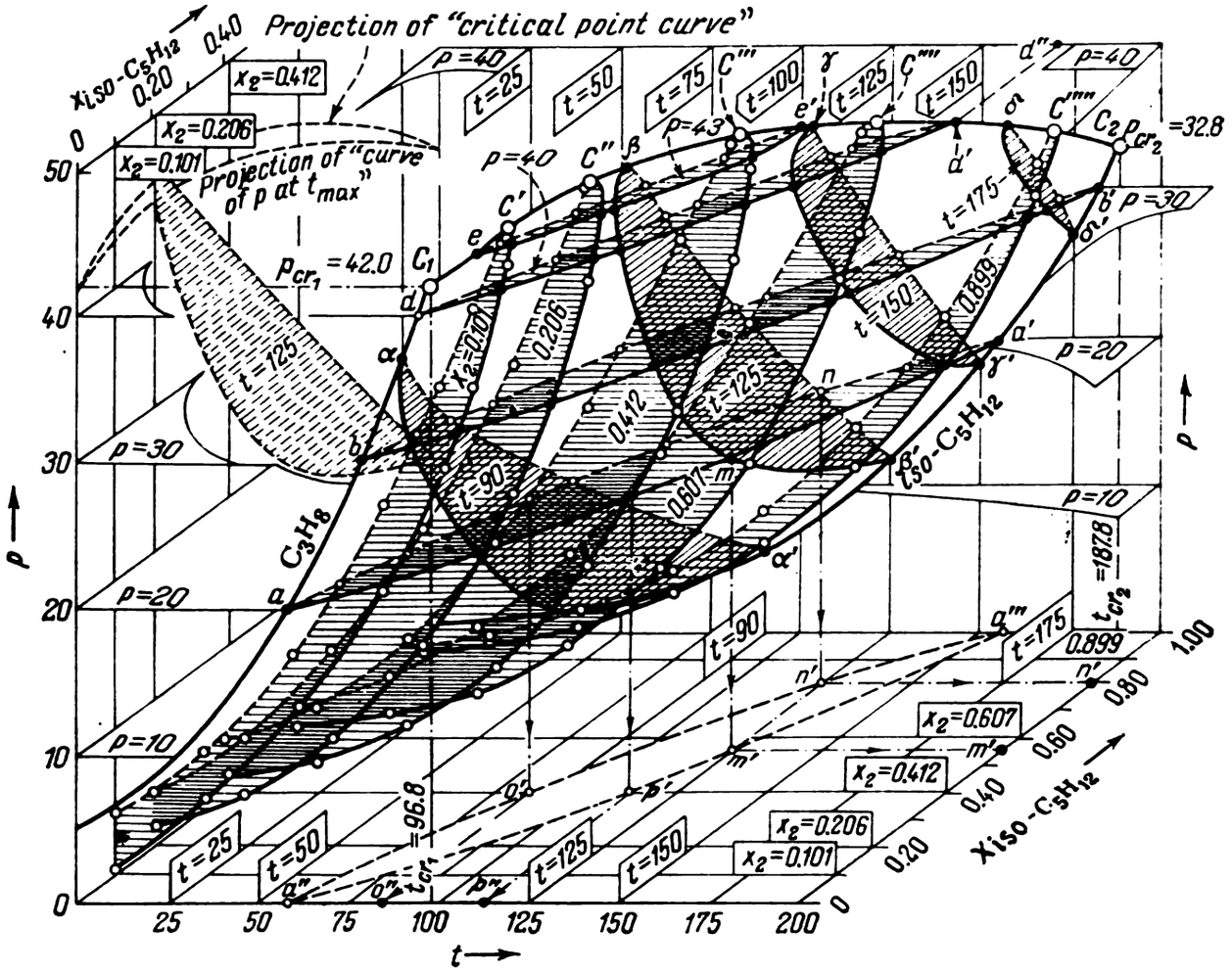

Fig. 111. Three-dimensional diagram of liquid-vapour equilibrium in the system propane-isopentane (the subscript "1" relates to C_3H_8, and "2" to *iso*-C_5H_{12}). Sections x = const (see Fig. 110), p = const (see Fig. 112), and t = const (see Fig. 113) are indicated

composition planes onto the plane of pure *iso*-C_5H_{12} are shown in Fig. 110.

Figure 111 also shows isobaric sections (p = 20, 30, 40 and 43 atm). One of the isobars (p = 20, plane *aa'*) has been projected onto the base of the drawing, i.e. onto the temperature-composition plane.

A projection of the isobars onto a horizontal plane is shown in Fig. 112, which also depicts the projection of the convolution point curve onto the plane p = const. At $p < (p^\circ_{cr})_{C_3H_8}$, the sections produce contours similar to contour *ama'n'a* in Fig. 112 (p = 20 atm). The curves of the contours extend to the planes of pure C_3H_8 and pure *iso*-C_5H_{12}, which confine the parallelepiped of Fig. 111. For pressures between $(p^\circ_{cr})_{C_3H_8}$ and $(p^\circ_{cr})_{iso\text{-}C_5H_{12}}$, the sections stop short of the surface *iso*-C_5H_{12} by a definite distance (for p = 40 atm, for example, by a distance of *d'd''*, see Figs. 111 and 112). This distance grows with increasing pressure. Finally, when $p > (p^\circ_{cr})_{iso\text{-}C_5H_{12}}$, the isobar planes reach neither of the confining planes (p = 43 atm).

Isothermal cross sections (t = 90, 125, 150 and 175 °C; in Fig. 111 they are indicated by diagonal hatching) form sections at right angles to the isobars. The section t = const at $t < (t^\circ_{cr})_{C_3H_8}$ (90 °C)

gives curves that extend up to both planes (section $\alpha\alpha'$). The section $t = 125\,°C$ already stops short of the plane $x_{C_3H_8} = 1$, because this temperature is higher than $(t^{\circ}_{cr})_{C_3H_8}$. Finally, at

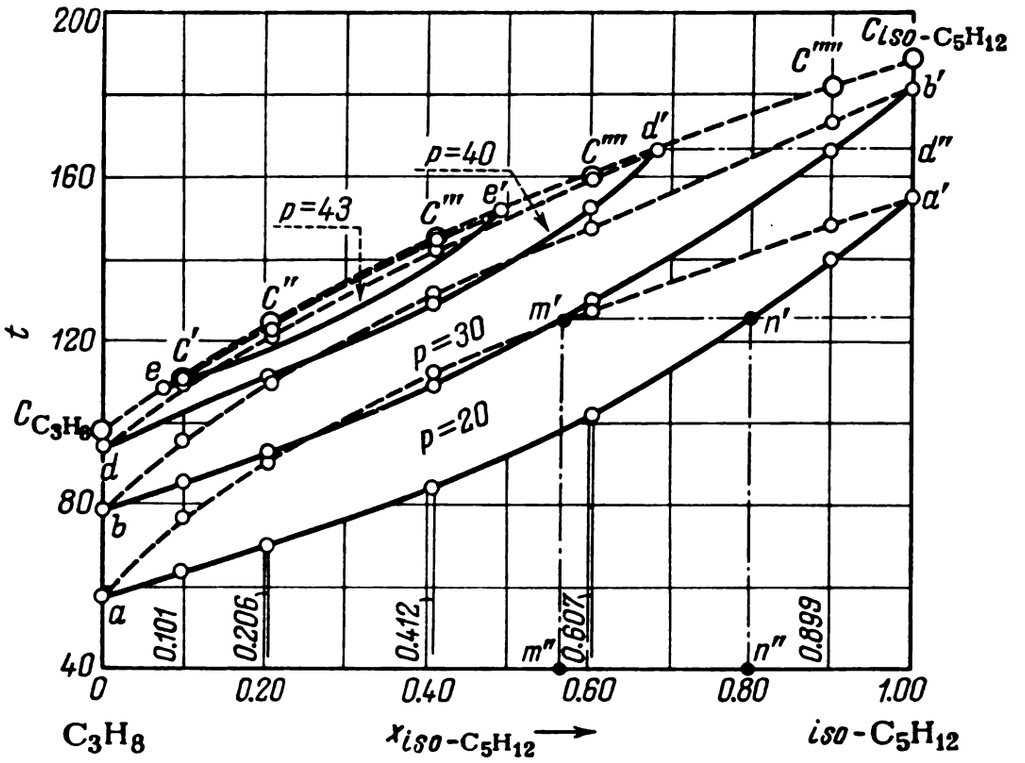

Fig. 112. Liquid-vapour equilibrium in the system propane-isopentane.
(Temperature-composition isobars)

$t = 175\,°C$, the interval of compositions corresponding to the coexistence of both phases becomes still less significant. A projection of the isotherms on the plane p-x is shown in Fig. 113, which also depicts the projection of the curves of the points p_{max} onto the plane $t = \text{const}$.

Any vertical line corresponding to a given composition of the system that is drawn in the graph of p against x through the heterogeneous region will in accordance with the lever rule divide an isobar-isotherm into lengths proportional to the amount of the coexisting phases. Hence, for example, it is simple to find the pressure at which the liquid fraction will be the maximum in the case of reverse condensation.

If we were to depict the isotherms for the given system in the coordinates $x^g = \varphi(x^{lq})$ for propane, then for a temperature below t_{cr} of both components we would get a customary curve connecting the corners of the diagram. Curves corresponding to isotherms above t_{cr}, however, in accordance with Fig. 111 would not reach the corner $x_{C_3H_8} = 1$.

The form of the sections x = const, p = const and T = const indicates the nature of the figure in the coordinates p-T-x corresponding to liquid-vapour equilibrium in a binary system. It (Fig. 111)

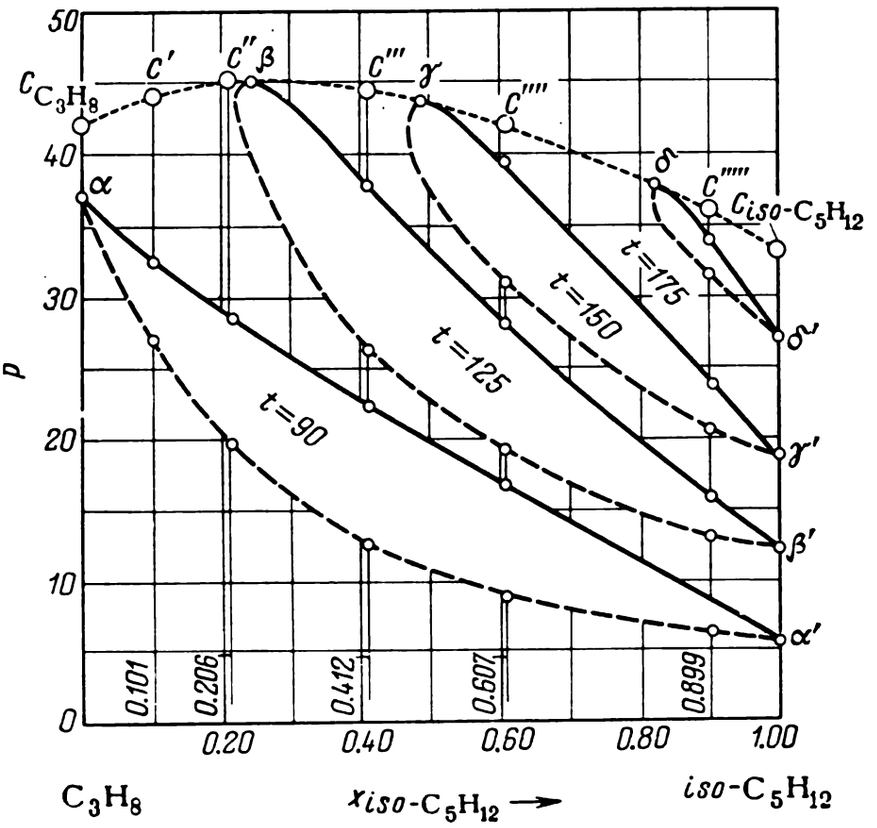

Fig. 113. Liquid-vapour equilibrium in the system propane-isopentane.
(Pressure-composition isotherms)

includes a heterogeneous region confined by two curved planes, one of which (the rounder and closest to us) characterizes the change in the composition of the vapour phase with a change in the temperature and pressure, while the other, shown by dashed lines, characterizes the composition of the liquid phase. These surfaces merge at the upper part of the figure, not at the very top, i.e. not along the curve of p_{max} and not along the line of t_{cr} (see, for example, Fig. 109), but along the critical points. To the scale of the illustrated drawings, the temperatures and especially the pressures on the critical curve and on the curve of the maximum pressure points coincide. In this example, the temperatures on the curve of the maximum temperature points are only slightly greater than the temperatures on the curve of the maximum pressure points (not over three kelvins), while the pressures are considerably lower than the maximum ones (the difference reaches two atmospheres). This is why the corresponding figures show only the critical curve. The figure in the coordinates p-T-x expands at the middle and narrows at the top. Its edges are the curves $p = \varphi(t)$ for the mixture components.

Figure 114 shows the dependence of the partition coefficients of C_3H_8 and *iso*-C_5H_{12} on pressure and temperature. The points of intersection of the isothermal loops at elevated temperatures by the horizontal lines $K = 1$ correspond to the critical pressures of

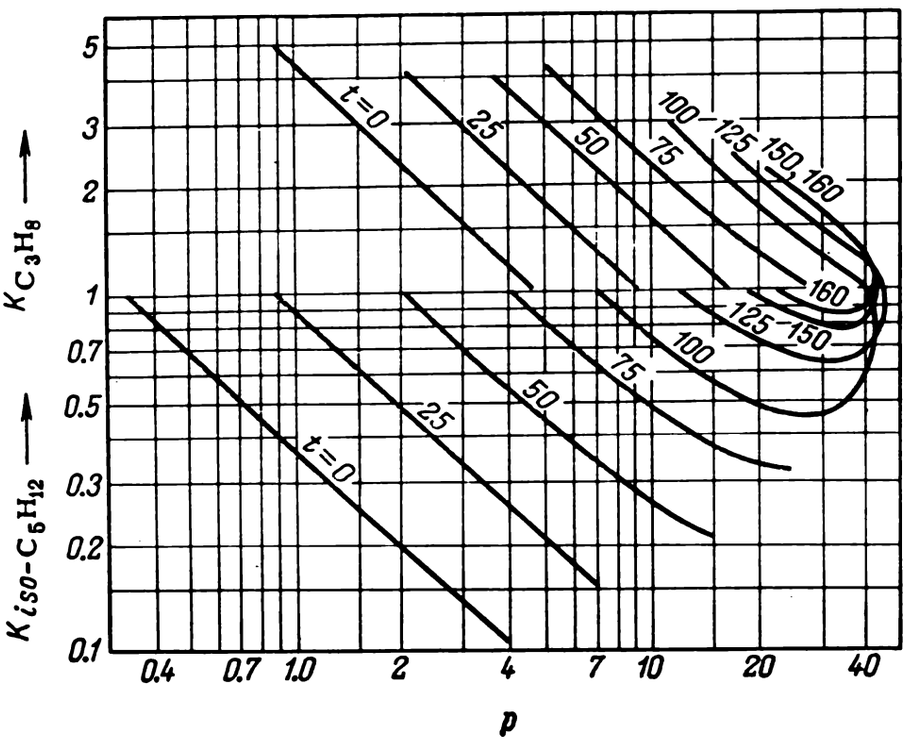

Fig. 114. Dependence of partition coefficients on pressure and temperature.
System propane-isopentane

the mixture, and at low temperatures to the saturated vapour pressure of the given component. The growth of K with increasing pressure is explained by reverse condensation.

This is not the only case. Thus, if the maximum pressure of a mixture coincides with the critical pressure of one of the components (for example the mixture N_2-O_2) then discontinuity in liquid-vapour equilibrium (and this distinguishes a binary system from a pure substance) is observed only at one end of the figure in the coordinates p-T-x, i.e. for mixtures rich in one of the components. When an extremum is present, the discontinuity will be in the middle part of the diagram. Systems are also known that are characterized by the presence of a temperature maximum and minimum on the critical curve.

Many important practical conclusions, in particular, the impossibility of separating mixtures of any composition at high pressures and temperatures, follow from the above. For distillation, either the pressure (temperature) must be lowered, or the composition changed. When gas-gas equilibrium can be brought about in a system (see Sec. 10.3), separation of the mixture becomes possible,

because when very high pressures are reached (above p_{cr}), it is possible to enter the region of a loop similar to that shown in Fig. 119 (p. 353).

Example 6. Use Fig. 111 to find the partition coefficients of propane and isopentane at $t = 125\,°C$ and $p = 20$ atm.

Solution. By projecting the line of intersection of the isothermal plane ($t = 125\,°C$) with the isobaric plane $p = 20$ atm (line mn) onto the plane t-x (see also Fig. 112, line $m'n'$), we get $x^{lq} = 0.80$ and $x^{g} = 0.56$ for *iso*-C_5H_{12}, whence $K = 0.56/0.8 = 0.7$ for *iso*-C_5H_{12} and $K = 0.44/0.2 = 2.2$ for C_3H_8.

Critical Temperatures and Pressures. The critical temperatures of a mixture of various hydrocarbons can be found according to the **Straus (1880)-Pavlevsky (1882) additivity rule:**

$$T_{cr} = \frac{g_1(T_{cr})_1 + g_2(T_{cr})_2}{100} \qquad (10.15)$$

where g_1 and g_2 are the weight or mass concentrations (in per cent) of the mixture components. Determination of the composition in per cent coincides better with experimental data than determination in mole fractions, although the results, as a rule, exceed the experimental data somewhat.*

No satisfactory method has yet been found for the *a priori* determination of p_{cr} for any substances.

It is obvious that

$$p_{cr} = (p_{cr})_2 + \frac{g_1}{100}[(p_{cr})_1 - (p_{cr})_2] + p_\Delta \qquad (10.16)$$

or

$$p_{cr} = (p_{cr})_2 + \frac{(T_{cr})_2 - T_{cr}}{(T_{cr})_2 - (T_{cr})_1}[(p_{cr})_1 - (p_{cr})_2] + p_\Delta \qquad (10.17)$$

where p_Δ is the deviation in the value of the critical pressure of a mixture from the additivity rule; the subscript 1 relates to the more volatile component (the first of these equations follows from Fig. 113, the second from Fig. 110).

Checking of experimental data shows that the quantity p_Δ reaches a maximum value for a composition close to 50% by weight, and a common curve is obtained for hydrocarbons of the methane series (Fig. 115).

* The critical temperature of a mixture of two liquids was first determined by O. Straus. He used Eq. (10.15) to calculate the critical temperature of water according to the critical temperatures of alcohol and an alcohol-water mixture.

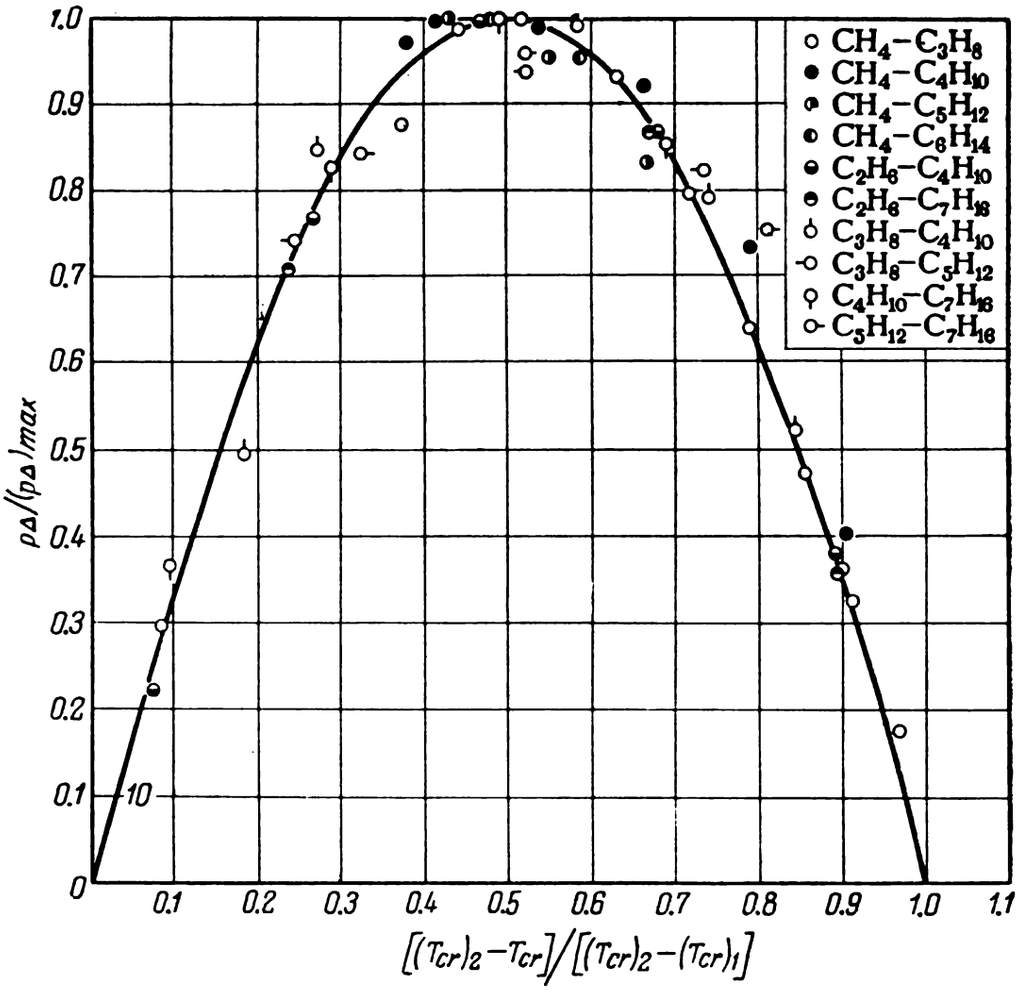

Fig. 115. Critical temperatures and pressures in binary mixtures of hydrocarbons

10.3. EQUILIBRIUM IN SYSTEMS WITH INCOMPLETELY MISCIBLE LIQUIDS

10.3.1. Liquid-Gas Equilibrium

Various kinds of liquid-gas equilibrium diagrams are obtained for liquids that mix only in a definite proportion. Two of them are shown schematically in Figs. 116 and 117.

Figure 116 relates to systems in which the vapour pressure over any mixtures is greater than that of the pure liquids. Curves *ac* and *db* (Fig. 116*a*) express the dependence of p on the composition of the system over unsaturated solutions, while curves *ae* and *be* correspond to the composition of the saturated vapour over them. Horizontal line *cd* connecting figurative points *c* and *d* of saturated solutions covers the interval of stratification; point *e* characterizes the composition of the vapour in equilibrium with coexisting saturated solutions *c* and *d*. Lines *cf* and *dg* characterize the mutual solubility of the liquids; in p-x coordinates, they are close to vertical

lines, because owing to the insignificant change in volume when the liquids dissolve, pressure has very little influence on the mutual solubility.

The same diagram with the same symbols is shown in Fig. 116*b* in *t*-*x* coordinates. Figure 116*c* depicts the relationship between

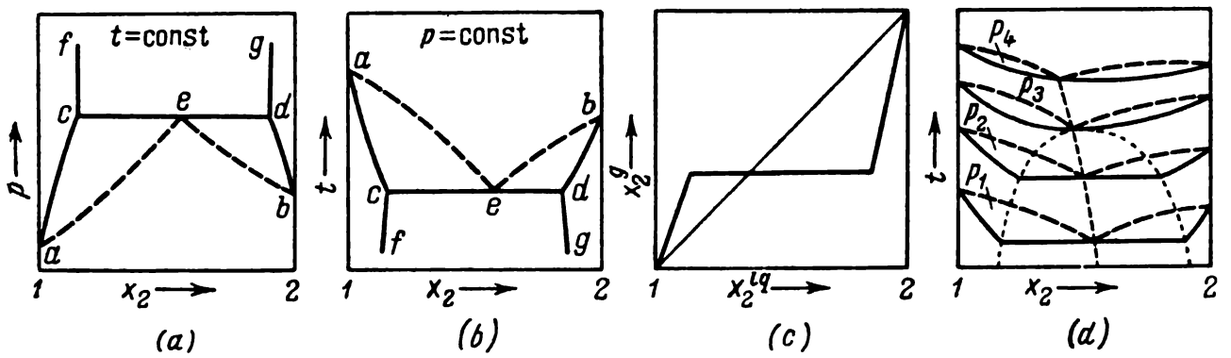

Fig. 116. Diagram of phase equilibria for systems consisting of incompletely miscible liquids (case I)

the composition of the boiling liquid and the dry saturated vapour. These systems are, as it were, a logical continuation of systems with a minimum boiling point; this can be clearly seen in Fig. 116*d*, where the dotted lines cover the region of stratification (see below).

Figure 117 shows a diagram for systems in which the vapour pressure over the mixtures is between p_1° and p_2°. Systems are known for which there is a maximum on section *db* of the boiling liquid isotherm. At this point, the curve $x_2^g = \varphi(x_2^{lq})$ intersects the diagonal. An example is a mixture of phenol with water. If in Fig. 116*d*

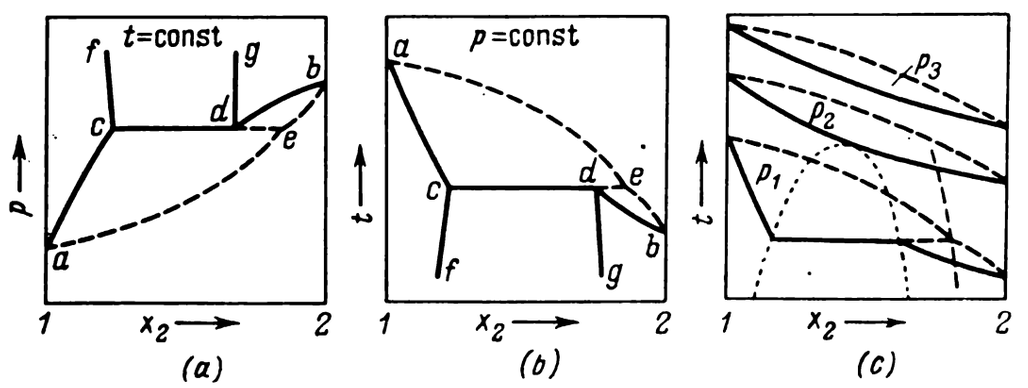

Fig. 117. Diagram of phase equilibria for systems consisting of incompletely miscible liquids (case II)

the point of the vapour composition is between the points of the composition of solutions, then in Fig. 117*c* it is beyond their limits.

In all cases, points *c*, *d* and *e* are on one horizontal line, because *the vapour pressures (total and partial) over conjugate solutions are the same* (Konovalov's rule).

Raoult's and Henry's laws can be used for guiding calculations of liquid-vapour equilibrium; the former is used for the substance present in excess, and the latter for the substance present in a smaller amount. The accuracy of the calculations grows when the mutual solubility of the liquids diminishes.

According to Konovalov's rule, for a solution rich in the first (I) and second (II) components we have

$$p_1 = K_1(x_1^{lq})_{II} = p_1^\circ(x_1^{lq})_I \quad \text{and} \quad p_2 = K_2(x_2^{lq})_I = p_2^\circ(x_2^{lq})_{II} \qquad (10.18)$$

It is also obvious that

$$p = p_1 + p_2 = p_1^\circ(x_1^{lq})_I + K_2(x_2^{lq})_I$$

and

$$p = p_1 + p_2 = p_2^\circ(x_2^{lq})_{II} + K_1(x_1^{lq})_{II}$$

Combining these equations with Dalton's law, we get

$$x_1^g = \frac{p - K_2}{p_1^\circ - K_2} \quad \text{and} \quad x_2^g = \frac{K_1}{p}\frac{p - p_2^\circ}{K_1 - p_2^\circ} \qquad (10.19)$$

After computing the values of K_1 and K_2 by Eq. (10.18), we can find the partial and total vapour pressures over mixtures of any composition, i.e. construct line *acdb* in Fig. 102*a*. Curve *aeb* of the dry saturated vapour is constructed using Eq. (10.19).

10.3.2. Liquid-Liquid Equilibrium

The mutual solubility of liquids at a constant pressure depends only on the temperature ($f_{cond} = 2 - 2 + 1 = 1$). Let us consider the growth in solubility with increasing temperature (Fig. 118), a result of positive values of the differential heats of solution of the liquids. Curve *aC* shows the solubility of the second liquid in the first, and curve *bC* the solubility of the first liquid in the second. Point *C*, at which the composition of both saturated solutions becomes identical, is called the **critical point of solution.*** At this point $f = 2 - 1 - 2 + 2 = 1$, and $f_{cond} = 0$. At $t > t_{cr}$, both liquids mix in any proportions. Curve *aCb* thus divides the entire diagram into two parts: the region below it corresponds to stratification, and that above it to homogeneous systems.

* D. Abashev was the first to study the mutual solubility of two liquids and its temperature dependence (1857). He also predicted the existence of a critical point and later investigated the dependence of the heat of solution on the nature of liquids. V. Alekseev described these systems, developed experimental procedures for their study and discovered the existence of critical points of solution (1875-1886).

The changes in the composition of the phases and the ratios between their amounts are shown for a mixture having composition *c*. When it is heated, the content of the phase that is a solution of the second liquid in the first will diminish, and at a temperature corresponding to point *t* it will equal zero, i.e. he system will become homogeneous.

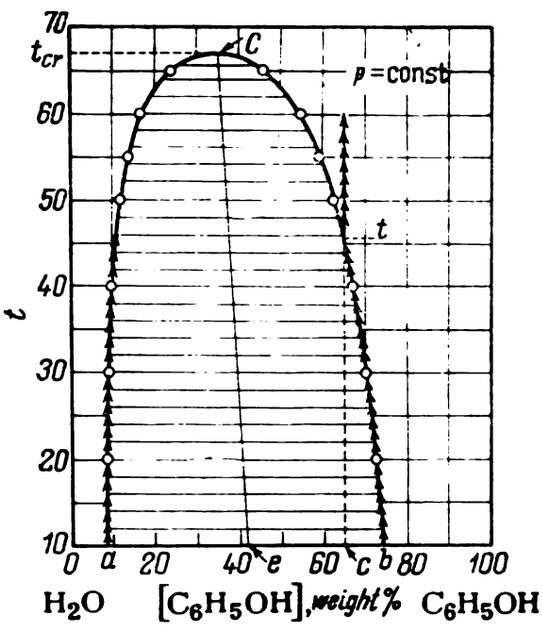

Fig. 118. Temperature-composition diagram for incompletely miscible liquids with an upper critical point. System water-phenol

According to **Alekseev's rule** (1886), also called **the rule of the straight diameter,** *the middles of the tie lines of a phase diagram form a straight line that terminates at the critical point of solution* (line *eC*). This rule allows us to supplement experimental data on the mutual solubility of liquids and also find the composition at the critical point according to the known value of t_{cr}. Alekseev's rule is approximate and most accurate when the composition is expressed in weight (mass) per cent.

There are also systems, in addition to those considered above, in which the solubility curve has a lower critical point, and systems in which this curve has both an upper and a lower critical points.

According to V. Semenchenko's theory, there is a similarity between the critical points of solution and the points of a second-order phase transition (see Sec. 7.7).

10.3.3. Gas-Gas Equilibrium

J. van der Waals long ago indicated the possibility of heterogeneous gas-gas equilibrium. These assumptions were confirmed experimentally, however, comparatively recently in the studies of I. Krichevsky, P. Bolshakov and D. Tsiklis [B108]. A limited mutual solubility of gases is observed at very high pressures, when the action of intermolecular forces becomes so significant that we can no longer speak of the energy independence of gases in a mixture*, and therefore the assumption of the unlimited mutual solubility of gases may become doubtful. These studies resulted in a number

* The great densities of highly compressed gases are an indirect confirmation of this circumstance. Thus, at $t = 65$ °C and $p = 15\,000$ atm, the density of gaseous hydrogen is almost twice the normal density of liquid hydrogen.

of interesting conclusions and made possible not only a general picture of phase equilibria in binary systems, but also the future practical use of this effect on separate gases.

The results of some of these experiments are presented by the isotherms in Fig. 119. A glance at the figure shows that at a given temperature a pressure exists below which gases mix without any limit (critical solution points *C*). At higher pressures, a homogeneous mixture becomes stratified into two phases. A growth in pressure results in stratification covering a constantly increasing interval of concentrations, in accordance with which the regions of mutual solubility narrow, and the composition of the equilibrium phases differs more and more. Thus, if we compress a mixture containing 57 mole per cent of NH_3 at $t = 100$ °C, then up to $p = 2600$ atm (point *C*) it will be homogeneous. A further growth in pressure leads to stratification, and, for example at $p = 5000$ atm, the mixture will consist of two phases containing 18 (point *a*) and 84.5 (point *b*) per cent of NH_3, respectively. If the composition of a mixture subjected to isothermal compression greatly differs from critical, then at the beginning of stratification both phases will immediately differ considerably in their composition. With elevation of the temperature, the region of stratification narrows and moves to high pressures, i.e. the pressure of the beginning of stratification rises; here the composition of the critical phases changes only slightly.

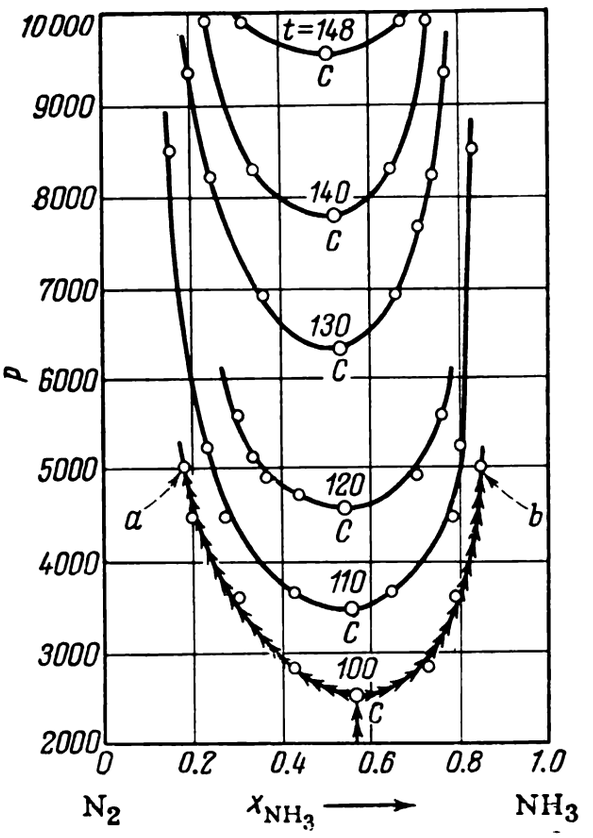

Fig. 119. Incomplete mutual solubility of gases.
Gas-gas equilibrium isotherms in the system nitrogen-ammonia

All these conclusions point to an analogy between the behaviour of gas mixtures at high pressures and of a liquid solution with incomplete mutual solubility at low temperatures, i.e. of a solution having an upper critical point. Each isotherm of Fig. 119 can be considered an "overturned" isobar of Fig. 118. Because of the obvious analogy in the action of a pressure increase and a temperature decrease, this is not a purely formal similarity. The similarity of the gas-gas equilibrium isotherms and the liquid-liquid equilib-

rium isobars makes it possible to use Alekseev's rule of the straight diameter to construct a gas-gas equilibrium curve. To find out whether or not there is a pressure above which stratification sets in, we must see whether a point of inflection having a horizontal tangent appears on the fugacity-mole fraction curve for the mixture at high pressures.*

Differentiating Eq. (8.9) with respect to the mole fraction of a component at p, T = const and equating the derivative to zero, we get

$$RT\left(\frac{\partial \ln f_i}{\partial x_i}\right)_{p,\,T} = \frac{RT}{x_i} + \int_0^p \left(\frac{\partial \overline{V}_i}{\partial x_i}\right)_{p,\,T} dp = 0 \qquad (10.20)$$

It follows from this equation that $(\partial \ln f_i/\partial x_i)_{p,\,T} = 0$ only when

$$\left(\frac{\partial \overline{V}_i}{\partial x_i}\right)_{p,\,T} < 0 \qquad (10.21)$$

Expression (10.21) is an essential and sufficient condition for the stratification of a mixture. Thus, in accordance with Le Chatelier's principle, decomposition into two gaseous phases is possible only for mixtures that are formed from the pure substances with an increase in volume.

It follows from Eq. (10.20) that stratification cannot set in either at $x_i \to 0$ or at $x_i \to 1$, because in the first case RT/x_i tends to infinity, whereas the derivative $(\partial \overline{V}_i/\partial x_i)_{p,\,T}$ retains a constant value (see Fig. 78*a*, p. 280); in the second case, although RT/x_i is minimum, $(\partial \overline{V}_i/\partial x_i)_{p,\,T}$ also tends to zero. Therefore, stratification is most probable in the "middle" regions of the concentrations.

Unfortunately, it is difficult to use Eq. (10.20) to calculate the pressure at which stratification sets in owing to the absence of numerical data on the derivatives $(\partial \overline{V}_i/\partial x_i)_{p,\,T}$ for very high pressures. It is possible only to assess the order of magnitude of this pressure very roughly, assuming that up to several thousands of atmospheres $(\partial \overline{V}_i/\partial x_i)_{p,\,T}$ = const.

Example 7. Determine the pressure at which a mixture of nitrogen and ammonia containing 53 volume per cent of NH_3 and having a temperature of 130 °C begins to decompose into two phases. Assume

* Omitting a precise substantiation of this criterion, we may indicate the analogy in the conditions of stratification of two- and one-component systems: the stratification of a pure gas into a liquid and a saturated vapour corresponds to a point of inflection having a horizontal tangent appearing on the pressure-volume isotherm [see Fig. 60 (p. 223) and Eqs. (7.10) and (7.11)].

that within the entire range of pressures from $p = 0$ to p_{cr} the value of $(\partial \bar{V}_2/\partial x_2)_{p,\,T} = -10$. Check the validity of this assumption on the basis of the experimental data given in Fig. 119.

Solution. Equation (10.20) yields

$$\frac{82.06 \times 403.2}{0.53} + \int_0^p (-10)dp = 0$$

or $62\,430 - 10p = 0$, whence $p = 6243$ atm. According to Fig. 119, the value of p is 6300 atm.

10.4. LIQUID-GAS EQUILIBRIUM FOR IMMISCIBLE LIQUIDS

This system is univariant. When both liquids are present, the composition and pressure of the vapour are determined only by the temperature and do not depend on the ratio between the components, and

$$p = p_1^\circ + p_2^\circ \tag{10.22}$$

(isotherm $a'b'$ in Fig. 120).

It goes without saying that absolutely immiscible liquids do not exist, because any liquids are soluble to a certain extent, i.e. mutually lower the vapour pressure. Therefore, line $a'b'$ should, first, be somewhat lower than shown in Fig. 120, and, second, should stop short of the axes of the pure components (see Fig. 116*a*). If the mutual solubility is negligible, these corrections have no practical significance.

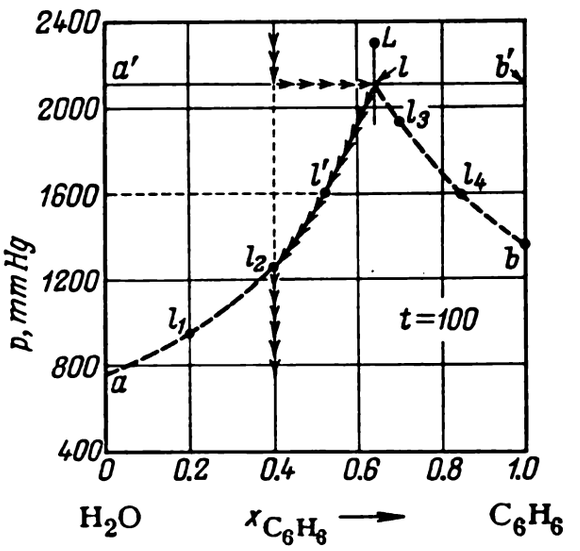

Fig. 120. Pressure-composition diagram of two immiscible liquids. System water-benzene

We shall consider that the vapour phase is a mixture of ideal gases. Consequently, in accordance with Dalton's law, its composition will be determined by the equations

$$x_1^g = \frac{p_1^\circ}{p_1^\circ + p_2^\circ} \quad \text{and} \quad x_2^g = \frac{p_2^\circ}{p_1^\circ + p_2^\circ} \tag{10.23}$$

Thus, for the system H_2O-C_6H_6 at $t = 100\,°C$, we have

$$x_{benz}^g = \frac{1350}{760 + 1350} = 0.64$$

i.e. the composition of the vapour in equilibrium at 100 °C with the water (point a') and the benzene (point b') will be depicted by point l. This means that if the pressure is lowered over a mixture of water and benzene having *any* composition at 100 °C, then when $p = 760 + 1350 = 2110$ mm Hg is reached, boiling will begin.

If the initial mixture has the same composition as the vapour formed (for example point L), then after isobaric evaporation of the entire mixture ($f_{cond} = 2 - 3 + 1 = 0$) the pressure will begin to lower ($f_{cond} = 2 - 1 + 1 = 2$), i.e. the vapour will become superheated. Upon isothermal compression of the vapour, these phenomena will proceed in the reverse sequence.

When the composition of the initial mixture differs from that of the vapour, the processes of evaporation (and condensation) will proceed differently: after the evaporation of both components (in the above example in the ratio 0.64 : 0.36), one of them remains in the liquid phase, and its evaporation simultaneously causes a change in the composition of the vapour and a decrease in the pressure ($f_{cond} = 2 - 2 + 1 = 1$). This will take place until the liquid phase disappears, after which the vapour becomes superheated at a constant composition. Thus, evaporation and condensation of such mixtures are characterized by the presence of a certain interval of pressures within which a pure liquid and a vapour mixture coexist.

The relationship between the pressure and composition of the vapour is expressed by Eqs. (10.23), which two curves correspond to. Thus, when $x_{benz} = 0.2$ and 0.4, water will be the surplus component, hence the pressure in the system will equal 760/0.8 = 950 mm Hg (point l_1) and 760/0.6 = 1265 mm Hg (point l_2), respectively. When $x_{benz} = 0.7$ and 0.85, the pressure in the system will equal 1350/0.7= 1930 mm Hg (point l_3) and 1350/0.85 = 1590 mm Hg (point l_4), respectively. Consequently, curves al and bl are the locus of the **dew points,** and line $a'lb'$ is the line of the beginning of condensation.

Thus, above $a'b'$ is the region of the liquid phase, below alb is the region of superheated vapour; $a'la$ is the region of a mixture of water and the vapour phase whose composition is determined by the intersection of the isobar with curve al; in region $b'lb$ liquid benzene coexists with a vapour mixture whose composition is determined similarly.

It should be noted that if a compressed mixture containing 40% of C_6H_6 is under a pressure of 2110 mm Hg, then after evaporation of the entire benzene from it (together with water in the ratio 0.64 : 0.36), the water begins to evaporate. Dilution of the vapour phase with water vapour changes its composition (along curve *la*). At a pressure of 1265 mm Hg, the liquid phase will vanish. Therefore, at a pressure below 1265 mm Hg, the points of the system coincide with the phase points. If the pressure were reduced, for example, only to 1600 mm Hg, there would be about 77% of vapour containing 52% of C_6H_6 in the mixture (point *l'*).

If we took a vapour containing 90% of C_6H_6 and subjected it to isothermal compression, then at a pressure of 1500 mm Hg condensation of the benzene would begin, i.e. the vapour phase would become enriched with H_2O (movement along curve *bl*); at point *l* the remaining vapour would condensate with an unchanging composition of the liquid.

Elevation of the temperature is attended by upward shifting of configuration *albb'a'*. The displacement of point *l* characterizing the composition of a mixture boiling together can be found by Vrevsky's first law (p. 328). If we take into consideration the influence of the temperature on the heat of vaporization of the components, then the calculations coincide well with experimental results, because owing to the mutual insolubility of the liquids, their heat of vaporization from mixtures equals that of the pure liquids.

To construct a temperature-composition diagram (Fig. 121), we plot the boiling points of the pure liquids t_1° and t_2° at the given total pressure p (points *a* and *b*). We then choose a temperature at which $p_1^\circ + p_2^\circ = p$. The boiling point of the mixture will be lower than t_1° and t_2°, since the total pressure is greater than the vapour pressure over each of the pure liquids. Thus, at $p = 760$ mm Hg, $t \approx 70$ °C, i.e. straight line *a'b'* is the boiling line. The content of benzene in the vapour at 70 °C will be 550/760 = 0.725 (point *l*). We construct curve *al* as follows. We select a number of temperatures between t_1° and t_2° and find p_1° and $p_2^\circ = p - p_1^\circ$. Next we calculate $x_2^g = p_2^\circ/p$. Similarly, we construct curve *bl* of the dew

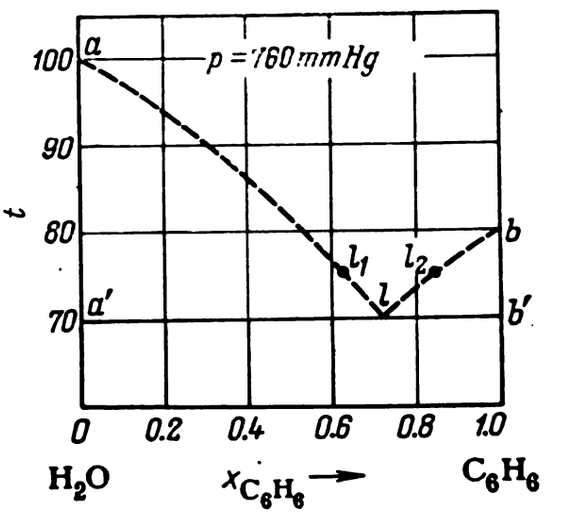

Fig. 121. Temperature-composition diagram for two immiscible liquids. System water-benzene

points of the second component. Thus, at $t = 75\,°C$, we have $p^\circ_w = 289$ mm Hg and $p^\circ_{benz} = 760 - 289 = 471$ mm Hg, i.e. $x^g_{benz} = 471/760 = 0.62$ (point l_1). Similarly, $p^\circ_{benz} = 648$ and $p^\circ_w = 760 - 648 = 112$ mm Hg, i.e. $x^g_{benz} = 648/760 = 0.85$ (point l_2). The resulting diagram is, as it were, an inverted image of Fig. 120.

We should note the obvious similarity between this diagram and the melting diagram of binary non-isomorphic systems (see Fig. 82, p. 289).

Chapter 11

EQUILIBRIUM IN THREE- AND FOUR-COMPONENT SYSTEMS

11.1. DEPICTING COMPOSITION

11.1.1. Three-Component Systems

Composition Triangle. The composition of a system is depicted by points on the plane of an equilateral triangle. Its apices correspond to the individual substances, the points on its sides to the relevant two-component systems, and the points inside the triangle to ternary mixtures (Fig. 122). Since the composition is generally expressed as a fraction or a per cent (mole fraction, or weight or mass per cent), the sides of the triangle are divided into 100 (or 10) parts, and straight lines parallel to the respective sides are drawn through the points of division.

The ratios of the components are determined either on the basis of the fact that the sum of perpendiculars dropped from any point onto the sides of an equilateral triangle equals its altitude, taken equal to 1 or 100 **(Gibbs's method),** or that the sum of lines drawn from any point inside an equilateral triangle parallel to its sides up to their intersection with another side of the triangle equals a side of the triangle, which is taken equal to 1 or 100 **(Roozeboom's method).**

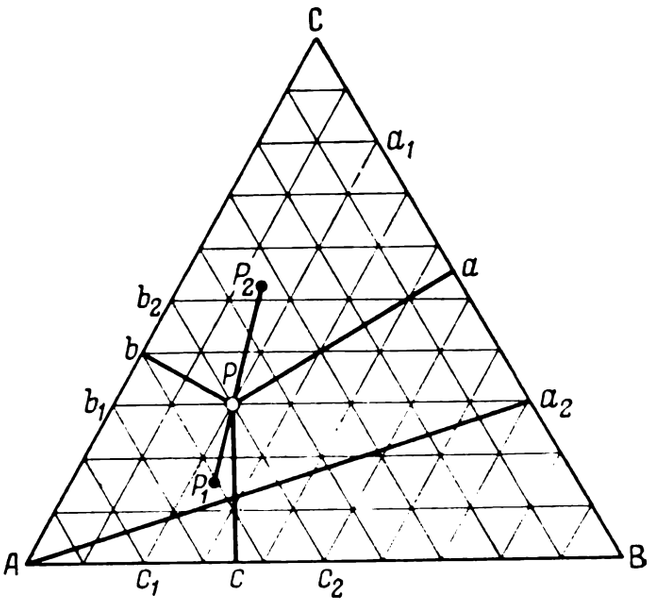

Fig. 122. Depicting the composition of three-component systems (composition triangle)

Thus, by the former method, the content of components A, B and C in the system which point P corresponds to is expressed by lengths Pa, Pb and Pc, respectively. According to the latter method, it is expressed by lengths $Pa_1 = Bc_2$, $Pb_1 = Ac_1$ and $Pc_2 = c_1c_2$ (or $Pc_1 = c_1c_2$, $Pa_2 = Bc_2$ and $Pb_2 = Ac_1$). Therefore,

system P contains 50% of substance A, 20% of B and 30% of C.

Both methods give the same result, since the sides and altitudes of an equilateral triangle are proportional to one another.

It is obvious that:

1. With a reduction in the concentration of a given component, the point characterizing the composition of the mixture shifts in a direction opposite to the apex corresponding to it (thus, shifting along Aa_2 toward a_2 indicates lowering of the content of A).

2. A straight line parallel to a side opposite to a given apex is a line of constant content of the component which this apex corresponds to (for example any point on line b_2Pc_2 corresponds to 50% of A).

3. A straight line passing through the apex of the triangle corresponding to a given component is a line corresponding to a constant ratio between the two other components * (for example at any point on line Aa_2 the ratio between B and C is 7 : 3).

4. If a given system is obtained from two others (decomposes into two others), then, as was the case for one- and two-component mixtures, the figurative points of all the systems are on one straight line (the **rule of straight tie lines**) and are arranged so that the ratio between the amounts of the two constituent systems is determined by the lever rule. For instance, if system P can be decomposed into systems P_1 and P_2 or obtained from them, point P must be on straight line P_1P_2, and

$$\frac{\text{amount of } P_1}{\text{amount of } P_2} = \frac{PP_2}{PP_1}$$

5. If a system is composed of three others, its figurative point should be at the centre of gravity (**centre of gravity rule,** a particular case of which is the lever rule).

Rectangular Coordinates. The origin of coordinates corresponds to component A. The concentrations of B in A and C in A [usually in grammes or in moles of substances B and C per 100 (1000) grammes or moles of substance A, or in per cent] are laid off along the axes of coordinates. A line passing through the origin of coordinates will be a line of a constant ratio between B and C.

This method of depicting the composition **(Schreinemacker's method)** is especially convenient for depicting systems that are dilute solutions. It is widely used in studying aqueous solutions of salts with a common ion (A = H_2O; B and C = salts) and is the

* This follows from the proportionality of perpendiculars dropped from any point of the line to the corresponding sides.

only possible method when the concentration of salts is related to a constant amount of water. Its practical advantage consists in the possibility of using conventional graph paper.

Although the rule of straight tie lines also holds here, the lever rule cannot be applied, because the points corresponding to pure B and C are (along the horizontal and vertical directions) at infinity. Consequently, the proportions given below that illustrate the application of the lever rule relate only to figures showing a composition triangle.

11.1.2. Four-Component Systems

The composition of systems consisting of three *common-ion* salts (for example the common-anion salts NaCl, KCl and $MgCl_2$) and water is depicted by a regular tetrahedron (Fig. 123), the length

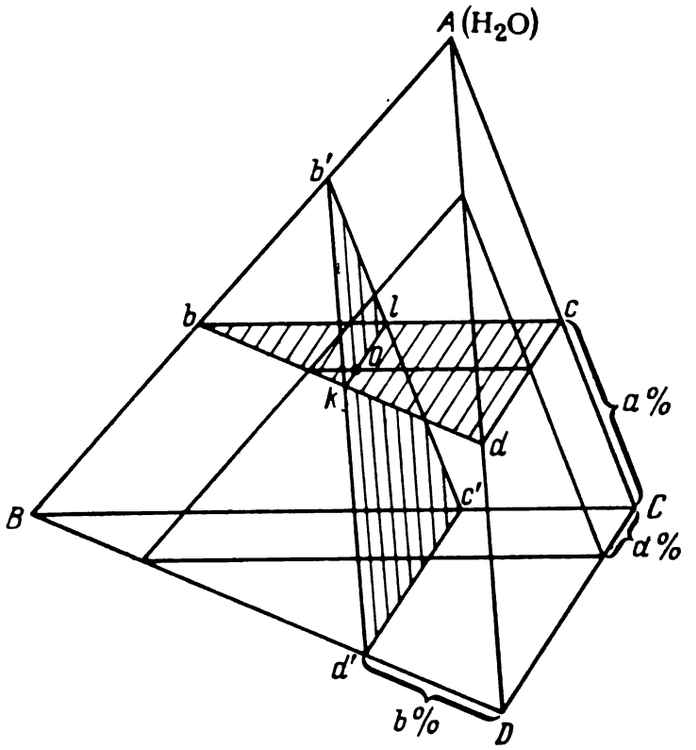

Fig. 123. Depicting the composition of four-component systems (three common-ion salts and water)

of whose edge is taken as 100%, and whose apices correspond to the pure substances (A = H_2O). Its edges depict the relevant binary systems, and its faces the ternary systems. Planes parallel to the faces correspond to systems containing a constant per cent of the substance opposite to this face. Thus, plane *bcd* corresponds to about 40% of A, and *b'c'd'* to about 30% of B. The lines of intersection of two such planes correspond to systems with a constant content of two substances. Thus, line *kl* corresponds to 40% of A and 30% of B. To find a point corresponding to a system of a

given composition, it is sufficient to lay off the content of B (in %) along edge AB in the direction from A to B, next lay off a length equal to the content of C from the obtained point downward in plane ABD parallel to AD, and then lay off a length equal to the content of D from the end of the previous line into the tetrahedron toward point C and parallel to BDC (the lengths may be laid in any sequence).

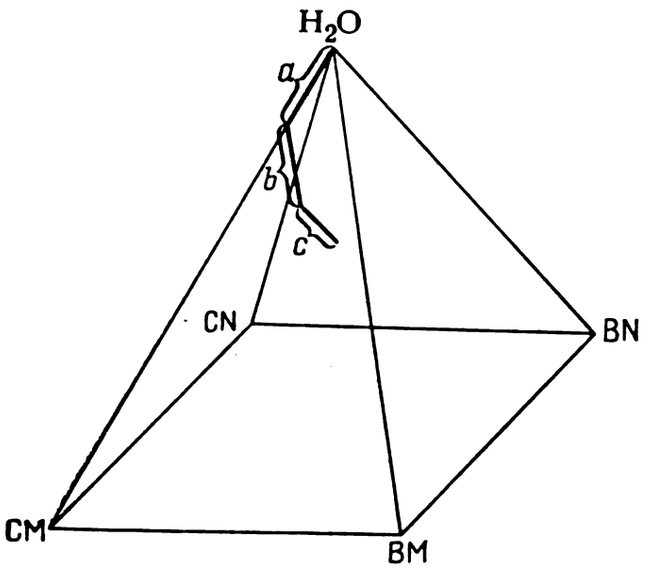

Fig. 124. Depicting the composition of four-component systems (mutual pairs of salts)

If salts having unlike ions are soluble in water ($BM + CN \rightleftharpoons BN + CM$ —**mutual pairs**), the composition is depicted by constructing a tetrahedral pyramid whose base is a square and whose faces are equilateral triangles (Fig. 124). The corners of the base correspond to the pure salts (mutual pairs are arranged on the same diagonal), and the vertex of the pyramid to water. The edges depict binary systems, the faces depict solutions of the corresponding salts in water, and the base — mixtures of the salts. Points inside the pyramid correspond to four-component systems. Owing to reaction [in Eq. (5.48) $q = 1$], the composition of the salt mass in such systems can be expressed by three salts. The amounts of the salts are expressed in equivalents, relating them to a constant amount of water (for example to 1000 moles). The point corresponding to a system having a given composition is found in the same way as for common-ion salts. In Fig. 124, lengths a, b and c express the number of gramme-equivalents of the salts CM, BM and BN in a constant amount of water, respectively. They are drawn parallel to the corresponding edges of the pyramid, length c being directed into it.

Here, as for binary and ternary systems, both the lever rule and the rule of the straight tie lines can be applied.

11.2. LIQUID-SOLID EQUILIBRIUM IN THREE-COMPONENT SYSTEMS

11.2.1. Substances Forming No Compounds

The melting diagram (**solubility polytherm**) is depicted in the form of a right trihedral prism whose base is a composition triangle, and along whose altitude the temperature is laid off (Fig. 125). Points a,

b and *c* are the melting points of the pure substances — A, B and C, respectively.* Freezing curves aE_1b, cE_2b and cE_3a for the binary systems are drawn on the faces of the prism. Since the addition of a third component lowers the melting point of a mixture of the

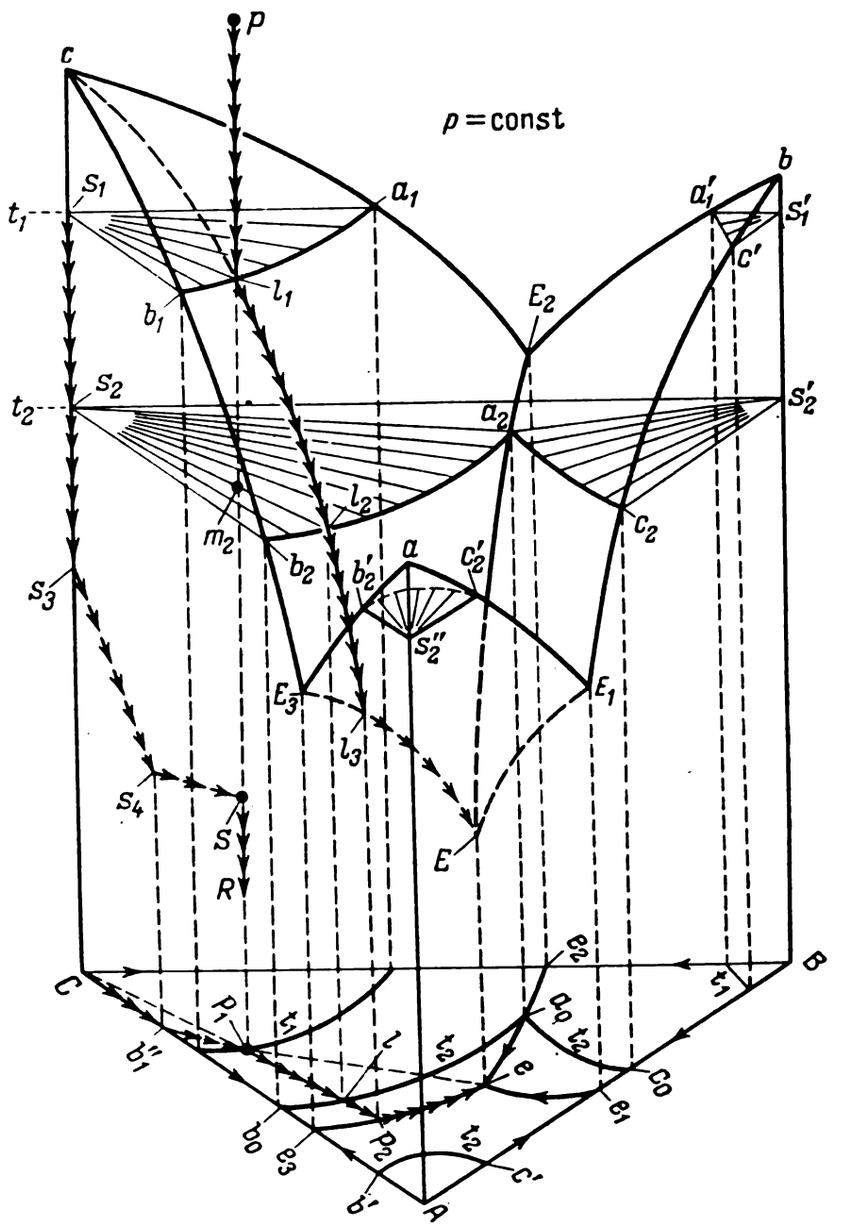

Fig. 125. Solubility polytherm of a mixture of three substances forming no compounds (schematic diagram)

other two, then, for example, the introduction of substance C into a eutectic mixture A + B (point E_1) lowers the freezing point, and we get curve E_1E running downward and into the prism and showing

* It is assumed as previously that the pressure which the system is under is greater than the vapour pressure over the liquid phase. Therefore, no equilibrium can set in between the vapour and the crystals, i.e. the gaseous phase is absent. The pressure is considered to be fixed.

"ternary solution-solid A + B" equilibrium. Curves E_2E and E_3E (also called **boundary curves**) are formed similarly. All of them converge at point E (the triple eutectic) at which the solution is saturated with all the components; this is the most low-melting mixture.

The freezing curves for the binary systems divide the saturation surface (the **liquidus surface**) into freezing fields of A, B and C (aE_1EE_3, bE_1EE_2 and cE_2EE_3, respectively), over which the liquid phase is. Since points E_1, E_2 and E_3 are at a different height, the volumes corresponding to heterogeneous systems are separated from the volumes corresponding to solid systems by an intricate surface (not shown in the figure). Below point E, the system will be solid with any ratio between A, B and C.

The freezing fields have been projected onto the base of the prism. The arrows show the cooling path. A change in temperature can be fixed by projecting onto the base the lines of intersection of the isothermal planes and the freezing fields drawn at different heights. To avoid overloading of the drawing, the isothermal sections are shown only for two temperatures t_1 and t_2 corresponding to the conditions that $(t_m)_A < t_1 > t_{E_2}$ and $(t_m)_A > t_2 < t_{E_2}$.

The entire region of the triangle in section t_2 consists of five fields: field $s_2a_2l_2b_2$ of equilibrium of crystals of C (point s_2) with solutions saturated with C (curve $b_2l_2a_2$ and its projection b_0la_0); field $a_2s_2'c_2$ of equilibrium of crystals of B (point s_2') with solutions saturated with B (curve a_2c_2 and its projection a_0c_0); field $b_2'c_2's_2''$ of equilibrium of crystals of A (point s_2'') with solutions saturated with A (curve $b_2'c_2'$ and its projection $b'c'$); field $s_2s_2''a_2$ of equilibrium of a mixture of crystals of C and B (line s_2s_2') with solutions of composition a_2 (in projection a_0) saturated with B and C; and a field of saturated solutions (between lines $b_2'c_2'$ and $b_2a_2c_2$, and in projection within contour $b'b_0a_0c_0c'$).

Let us consider the cooling of an unsaturated solution such as P. The system is trivariant ($f_{cond} = 3 - 1 + 1 = 3$), and its figurative point is therefore inside of the prism (the temperature and concentration of two substances can be varied *). In the conditions which point $l_1(P_1)$ ** corresponds to, freezing of C will begin, and the system will become bivariant. In connection with the freezing out of C, the concentration of A and B in the liquid phase will grow, while the freezing point will lower; hence, the figurative point will begin to move downward from l_1 along plane cE_2EE_3. In accordance with the unchanging ratio of A to B in the liquid phase, its trajectory

* The concentration of the third substance is not an independent variable.

** Here and below the corresponding symbols in the projection onto the base of the prism (or pyramid) are indicated in parentheses.

will be on the continuation of straight line $cl_1(CP_1)$, i.e. C will freeze in conditions which freezing path $l_1l_2l_3(P_1lP_2)$ corresponds to. In the course of freezing, the change in the state of the solid phase will be characterized by points on vertical line $s_1s_2s_3$. The ratio between the phases is determined by the lever rule. Thus, at t_2 (system point m_2)

$$\frac{\text{amount of frozen C}}{\text{amount of remaining solution } l_2} = \frac{m_2l_2}{m_2s_2} = \frac{P_1l}{CP_1}$$

In the conditions which point $l_3(P_2)$* corresponds to, the solution will also become saturated with respect to A, i.e. A will freeze out together with the continuing freezing of C. In the process of joint freezing of C and A, the change in the composition of the solid corresponds to line $s_3s_4(cb_1'')$, while the composition of the liquid phase corresponds to line $l_3E(P_2e)$. At this stage of cooling, the system is univariant: a single composition of the liquid phase corresponds to each temperature, and the figurative point will accordingly be on the curve. When point E corresponds to the composition of the liquid phase, the solution will be saturated with all the components, and the remaining liquid will freeze without a change in its composition; the system becomes invariant, i.e. characterized by single values of the temperature and concentration of the components. In the last stage of freezing, the figurative point of the solid will move from point s_4 on a face of the prism to point $S(P_1)$ inside it.** At point S, the system will be completely frozen, i.e. univariant. Its figurative point (S) will again be on the vertical line corresponding to the initial composition. Therefore, a further removal of heat cannot result in a change in the phase composition, and only lowers the temperature (line SR).

The freezing points of the consecutively freezing components and the ratios between the amounts of the phases are determined by the composition of the initial mixture. If it had such a composition that the projection of the point corresponding to it would be on isotherm t_1 beyond the point of intersection of this isotherm with straight line Ce, freezing of C would be followed by freezing out of B. If the projection of the point characterizing the initial system were on the line connecting point A (or B, or C) to point e, then after the relevant component freezes, the remaining liquid would freeze without a change in its composition, and so on.

The above diagrams are constructed according to experimental data. For ideal solutions (for example for hydrocarbon mixtures),

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* It is obvious that $Cs_3 = P_2l_3$.

** It is clear that $b_1''s_4 = P_1S = eE$, i.e. the straight line is parallel to the base of the prism (it is an isotherm).

they can be constructed on the basis of the values of the melting points and heats of fusion of the components using Eq. (9.3)

$$\left.\begin{aligned} \log (x_1)_T &= \frac{(\Delta H_f)_1}{4.576}\left[\frac{1}{(T_m)_1} - \frac{1}{T}\right] \\ \log (x_2)_T &= \frac{(\Delta H_f)_2}{4.576}\left[\frac{1}{(T_m)_2} - \frac{1}{T}\right] \\ \log (x_3)_T &= \frac{(\Delta H_f)_3}{4.576}\left[\frac{1}{(T_m)_3} - \frac{1}{T}\right] \end{aligned}\right\} \qquad (11.1)$$

The value of T (in particular T_e) can be determined by the method of consecutive approximations: taking a value of the temperature that is lower than the melting point of the most low-melting substance and inserting it into these equations, we find the mole fractions of the components. After obtaining values of Σx_i for various temperatures, we use graphical interpolation to find the value of T at which $\Sigma x_i = 1$. This will be the needed value.

For practical purposes, it is more convenient to consider not the projection of the polytherms, but isothermal sections (see the following pages).

11.2.2. Substances Forming Compounds

If the substances form compounds (hydrates, double salts, etc. in the case of aqueous solutions), new freezing fields will appear in the diagram and on its horizontal projection. Their number will equal that of the new solid phases.

Thus, if two of the three components form a single compound (for example when salts B and C form double salt D in water — component A), the diagram will have the form shown in Fig. 126*a*

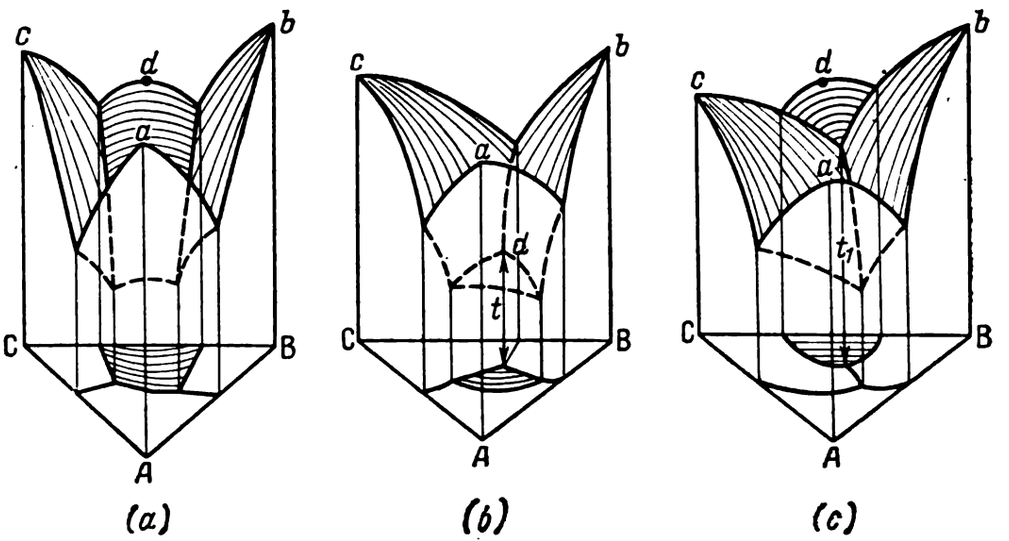


Fig. 126. Variants of a solubility polytherm for a mixture of three components forming a double salt

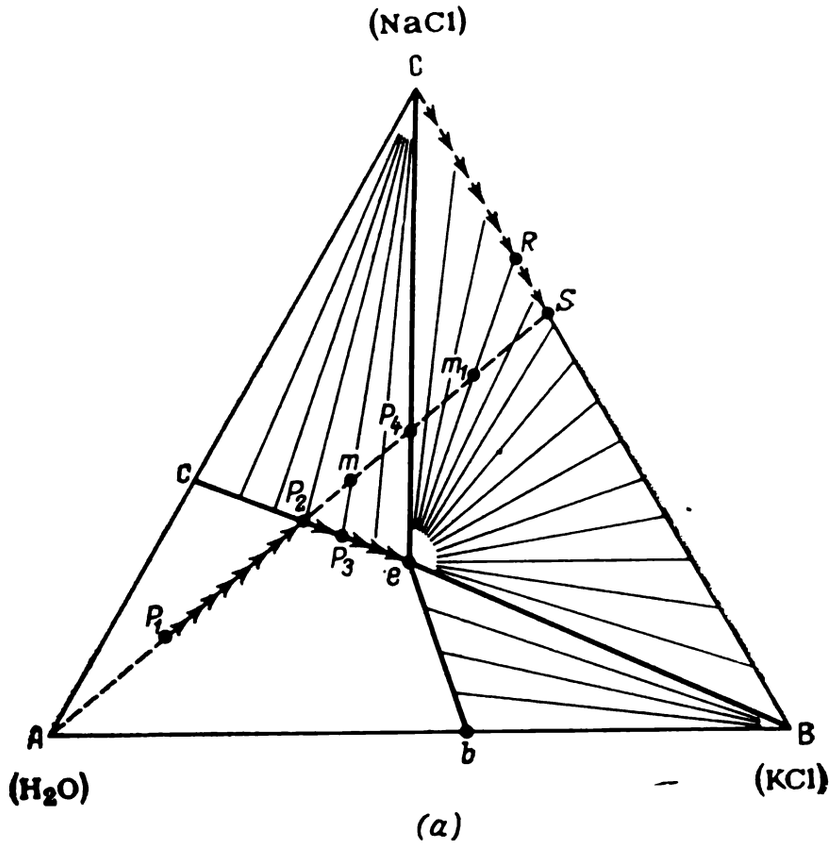
(the double salt is stable within a broad interval of temperatures — from the cryohydrate temperature to the points of joint melting with anhydrous salts), 126*b* (the double salt is stable up to a certain temperature t), or 126*c* (the double salt is stable from a certain temperature t_1 to the points of joint melting with anhydrous salts). Consequently, in the first case upon evaporation of the solution of the double salt, the point on the vertical line corresponding to its composition gets into the freezing field of the double salt in all conditions. In the second and third cases, this occurs at low and high temperatures, respectively. Above t in the second case and below t_1 in the third, isothermal evaporation will cause a pure component to freeze (see below).

11.2.3. Isotherms of Aqueous Solutions of Two Common-Ion Salts

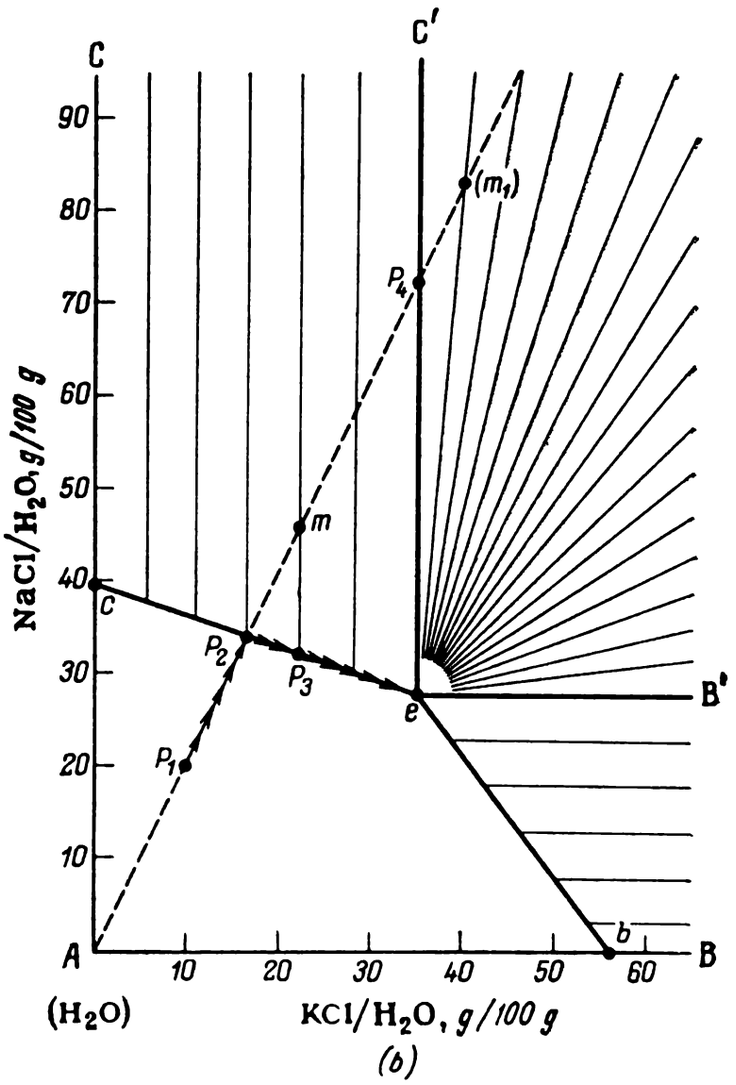
The Substances Do Not React. Figure 127 depicts isotherms of the solubility of salts (with a common ion) that do not form a compound with each other or with water, using the system H_2O-NaCl-KCl as an example. This diagram coincides with the drawing obtained when an isothermal section is drawn through the prism of Fig. 125 on the condition that C and B are salts, A is water, and the isotherm is below the salt-salt eutectic point, but above the freezing point of water. If the latter condition is not observed, and $t < 0$, a field of ice will appear in the triangle at apex A (H_2O), and an isotherm coinciding with that shown in Fig. 125 for t_2 will be obtained.

Points b and c express the solubility of the salts in water. Solubility curves be and ce show the changes in the concentration of solutions saturated with B and C, respectively, in the presence of the other salt when its content grows. It can be seen from the direction of the curves that the addition of one salt to a saturated solution of the other salt results in partial freezing of the latter. If the salts did not mutually affect the solubility, lines ce and be would be parallel to the corresponding sides of the concentration triangle. An increase in solubility is encountered comparatively rarely; it may be due, for instance, to the formation of a complex ion. Point e [a_2 (a_0) in Fig. 125] characterizes the composition of a solution saturated at the given temperature with both salts. N. Kurnakov and S. Zhemchuzhnov suggested calling it the **eutonic * point** (1919). The origin of this term is explained by the fact that at this point the vapour pressure over the system is minimum, because the total concentration of the solutes is maximum.

* From the Greek "eu" — easily and "tonikos" — stretching.



(a)



(b)

Fig. 127. Isotherm of solubility in water of two common-ion salts not reacting with each other in triangular (*a*) and rectangular (*b*) coordinates. System H_2O-NaCl-KCl, $t = 100$ °C. (See Example 1)

Regardless of the initial composition, the terminal point of freezing will be point *e*. Its similarity with the eutectic point also consists in that at this point $f = 3 - 4 + 2 = 1$ and at a constant temperature $f_{cond} = 0$.

Any point within contour *Aceb* corresponds to unsaturated solutions; fields *beB* and *cCe* in Fig. 127*a* and, accordingly, the fields to the right of curve *eb* and above curve *ce* and limited by the corresponding parallel straight lines *bB* and *eB'*, *cC* and *eC'* in Fig. 127*b* are mixtures of the corresponding salt and its saturated solution; finally, region *CeB* (Fig. 127*a*) and accordingly *C'eB'* (Fig. 127*b*) correspond to a mixture of solutions saturated with both salts with a different surplus of them in the solid phase.

The thin straight lines in these and following figures depict tie lines. They have been drawn in all the heterogeneous regions and allow us to assess the change in the composition of the phases and in the ratio between their amount at any point of the system, and thus at every moment of the process of isothermal evaporation. Their direction in the regions of equilibrium between the solid and liquid phases in Fig. 127*b* is due to the fact that the points corresponding to pure salts are at infinity on the axes of coordinates. Thus, the points of a mixture of a solid salt and a saturated solution, in accordance with the rule of the tie lines, are on one straight line.

Let us consider the isothermal evaporation of an unsaturated solution (for example of mixture P_1).

Since no freezing occurs up to saturation of the solution, the ratio between the salts does not change. Therefore, the first stage of the process will be shown by a straight line that is the continuation of line AP_1. When the solution has the composition P_2, it will become saturated, and C will begin to freeze out from it. At this moment, the ratio between the amounts of evaporated water will be $P_1P_2 : AP_1$.

Upon further evaporation, the composition of the system will be characterized by points on the continuation of evaporation line AP_2. They will already correspond to heterogeneous systems — mixtures of solid C and a solution saturated with it. Because of the fact that freezing out of C results in enrichment of the solution with salt B, the phase point of the solution will shift from P_2 to *e*, and the points of the system from P_2 to P_4. The composition of the system will be depicted by the point of intersection of the straight line of evaporation and the corresponding tie line on whose moving end the phase point of the saturated solution is situated. Thus, when the latter reaches P_3, the composition of the system will be depicted by point *m*, the ratio between the amounts of the solution and the frozen-out salt being $Cm : mP_3$, and that between the amounts of evaporated water and the remaining mixture being $mP_1 : P_1A$.

When the point of the system reaches P_4, and the phase point, eutonic point e, the solution will also become saturated with salt B. After this, simultaneous freezing of both salts will begin in the same ratio as that in which they are found in the remaining solution. (At this moment the ratio of the amount of solution to the amount of frozen-out C will be $CP_4 : P_4e$.) The amount of solution e, while retaining a constant composition, will diminish. The composition of the solid mixture will be depicted by points on straight line CB. If further dehydration is discontinued at the moment when the composition of the salt mixture is characterized by point R, i.e. the ratio between the amounts of frozen-out salts will become equal to $RB : CR$, the point of the system will be at m_1, while the fraction of the solid phase will be expressed by m_1e/Re. The ratio between the amounts of the three phases at point m_1 can be found by the rule of the centre of gravity.

At point S, the mixture will be completely dehydrated. This can be seen from two coinciding features: (1) component A (H_2O) is absent on side BC; and (2) the arm of the liquid phase on the tie line becomes equal to zero when point S is reached.

It is also simple to follow the evaporation of a solution rich in B.

If the initial point were on the line connecting points A and e, then upon evaporation of an unsaturated solution simultaneous freezing of both salts would occur, and the ratio between the amounts of the freezing-out salts would always be constant and equal to their ratio in the initial solution.

Example 1. The solubilities of NaCl and KCl in water at 100 °C are 39.4 and 56.2 g, respectively, while their joint solubility is 27.39 g of NaCl + 35.16 g of KCl (per 100 g of water). Construct a phase diagram (considering the solubility lines to be straight) and find for a solution containing 10 kg of KCl, 20 kg of NaCl and 100 kg of H_2O subjected to evaporation at 100 °C:

(1) the amount of evaporated water and the composition of the final solution (a) before the appearance of the solid phase; and (b) before the beginning of freezing out of both salts;

(2) the amount of frozen-out salts and the composition of the solution remaining after the removal of 95% of the water contained in the initial solution;

(3) the amount of KCl that must be added to the initial solution for evaporation of the water to result in simultaneous freezing out of both salts.

Solution. We use the above data to construct a solubility diagram (Fig. 127).

The initial solution contains $[10/(10 + 20 + 100)] \times 100 = 7.7\%$ of KCl, 15.4% of NaCl and 76.9% of H_2O, i.e. its state is depicted by point P_1.

1. (a) To find the amount of evaporated water (before freezing begins), we connect points P_1 and A and continue this line until it intersects line *ce*. In Fig. 127, we find that the solution at point P_2 will have the composition: 34% of NaCl, 17% of KCl and 49% of H_2O. Since no salts froze out during evaporation, then

$$\frac{[\text{NaCl}],\ \%\ \text{at}\ P_2}{[\text{H}_2\text{O}],\ \%\ \text{at}\ P_2} = \frac{34}{49} = \frac{20}{y}$$

or

$$\frac{[\text{KCl}],\ \%\ \text{at}\ P_2}{[\text{H}_2\text{O}],\ \%\ \text{at}\ P_2} = \frac{17}{49} = \frac{10}{y}$$

whence we find that the solution will contain $y = 28.8$ kg of H_2O, i.e. a saturated solution will contain 10 kg of KCl, 20 kg of NaCl and 28.8 kg of H_2O, while $100 - 28.8 = 71.2$ kg of H_2O will evaporate (before freezing begins).

(b) In Fig. 127 we find that the solution at the eutonic point will consist of 27% of NaCl, 35% of KCl and 38% of H_2O. Since no potassium chloride froze out up to the composition corresponding to the eutonic point, then

$$\frac{[\text{KCl}],\ \%\ \text{at}\ e}{[\text{H}_2\text{O}],\ \%\ \text{at}\ e} = \frac{35}{38} = \frac{10}{y}$$

whence the amount of water at the eutonic point $y = 10.8$ kg, i.e. in the process of freezing out of NaCl the amount of water evaporated will be $28.8 - 10.8 = 18.0$ kg.

The amount of NaCl that has not frozen out will be determined from the proportion

$$\frac{[\text{KCl}],\ \%\ \text{at}\ e}{[\text{NaCl}],\ \%\ \text{at}\ e} = \frac{35}{27} = \frac{10}{y}$$

i.e. $y = 7.7$ kg of NaCl; the solid will contain $20 - 7.7 = 12.3$ kg of NaCl, i.e. 61.5% of the initial amount of the NaCl.

Thus, at the moment when KCl begins to freeze out (point *e*), the solution will consist of 10.8 kg of H_2O, 10 kg of KCl and 7.7 kg of NaCl.

2. The amount of water remaining is $100 - 95 = 5$ kg.

In the given case, unlike the ones considered above, the content of all the components changes, but since the composition of the eutonic solution remains unchanged, then

$$\frac{[\text{NaCl}],\ \%\ \text{at}\ e}{[\text{H}_2\text{O}],\ \%\ \text{at}\ e} = \frac{27}{38} = \frac{y}{5}$$

i.e. $y = 3.5$ kg of NaCl will remain in the liquid phase, and $7.7 - 3.5 = 4.2$ kg of NaCl will freeze out upon evaporation of the eutonic mixture.

Similarly

$$\frac{[KCl],\ \%\ \text{at}\ e}{[H_2O],\ \%\ \text{at}\ e} = \frac{35}{38} = \frac{y}{5}$$

i.e. $y = 4.6$ kg of KCl will remain in the solution, and $10 - 4.6 = 5.4$ kg of KCl will freeze out upon evaporation of the eutonic mixture.

Consequently, at the end of evaporation, the solid phase (point R) will consist of $12.3 + 4.2 = 16.5$ kg of NaCl and 5.4 kg of KCl, i.e. of 75% of NaCl and 25% of KCl; the liquid phase (point e) will consist of 5 kg of H_2O, 3.5 kg of NaCl and 4.6 kg of KCl (check: 38% of H_2O, 27% of NaCl and 35% of KCl), while the ratio between them according to the lever rule will be

$$\frac{c}{lq} = \frac{16.5 + 5.4}{5 + 3.5 + 4.6} = \frac{1.67}{1} = \frac{em_1}{m_1R}$$

i.e. the composition of the mixture will be depicted by point m_1.

3. To solve this problem, it is necessary that the composition of the solution be depicted by a point on the straight line connecting apex A (H_2O) to the eutonic point. Since only KCl is added to the initial solution, the required point should at the same time be on the straight line connecting point P_1 to apex B. Consequently, the position of the required point is determined by the intersection of lines Ae and P_1B. Its coordinates are 13.5% of NaCl, 19% of KCl and 67.5% of H_2O.

Seeing that

$$\frac{[NaCl],\ \%}{[KCl],\ \%} = \frac{13.5}{19} = \frac{20}{y}$$

the amount of KCl in the final solution (y) will be 28 kg, i.e. it is necessary to add $28 - 10 = 18$ kg of KCl to the initial solution.

One of the Salts Forms a Crystallohydrate. We shall consider a stable and an unstable crystallohydrates.

1. If a crystallohydrate (denoted by H) is stable, the solubility isotherm will acquire the form shown in Fig. 128.

This diagram can be considered as one of a very simple kind (Fig. 127*a*), in which triangle ACB has been replaced by triangle AHB and supplemented with field HCB of equilibrium of the solid anhydrous salts and the crystallohydrate. The diagram in rectangular coordinates (Fig. 128*b*) differs from the one in Fig. 127*b* in that point H will be at a point corresponding to the concentration

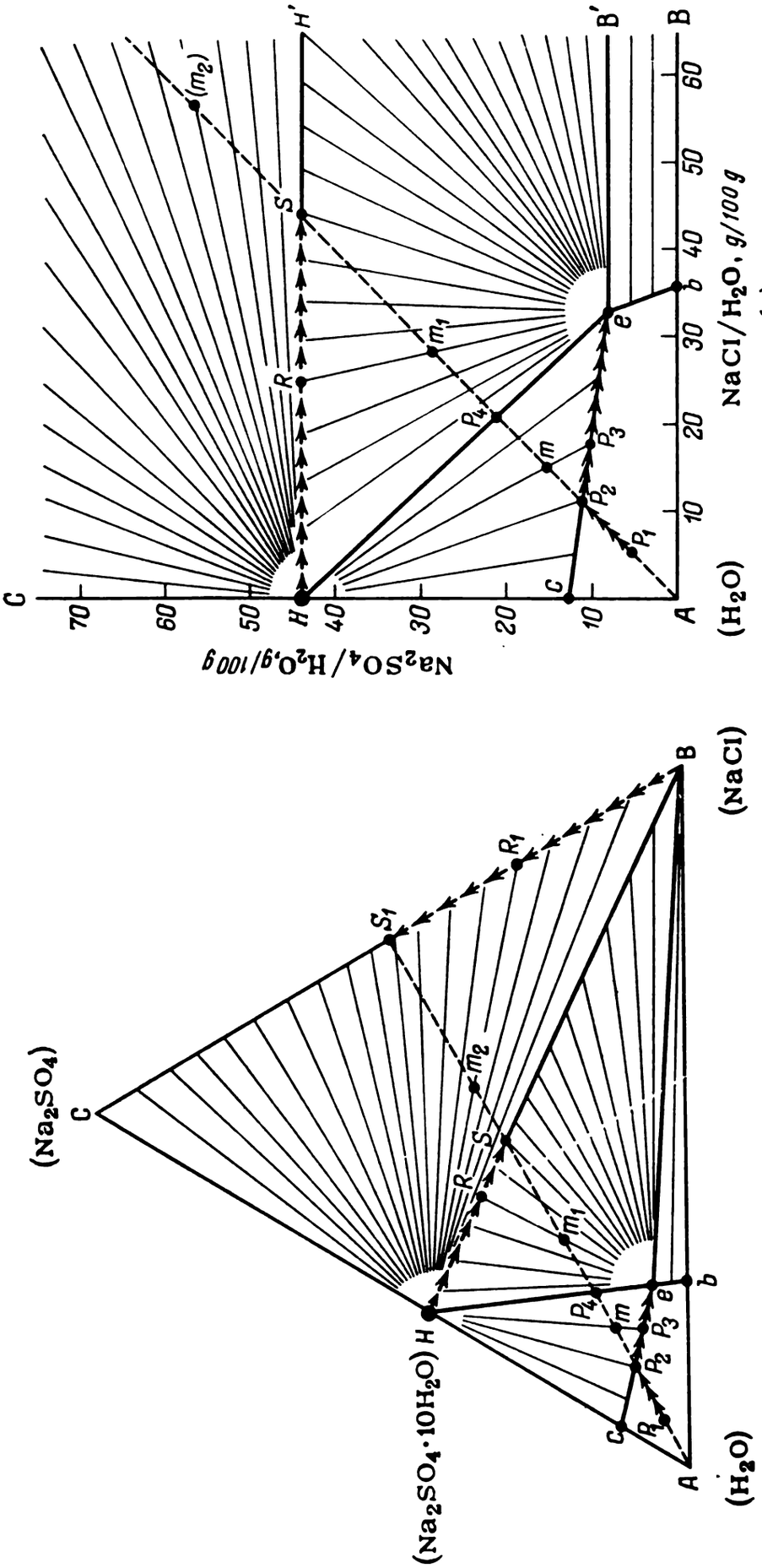


Fig. 128. Isotherm of solubility in water of two common-ion salts, one of which forms a stable crystallohydrate.
System H_2O-Na_2SO_4-NaCl, t = 15°C. (See Example 2)

of C in the crystallohydrate instead of being at infinity. Therefore, the region of freezing of the crystallohydrate is limited from above by line *He* forming not a right angle, but an obtuse angle (*HeB'*), while the regions of freezing of B and C are divided by a field of joint freezing of B and H (*H'HeB'*).

Solution P_1 will evaporate up to point S similarly to the evaporation of a solution of salts not reacting with water (see Fig. 127), the only difference being that H will freeze out instead of C, first in the pure state (within the interval P_2P_4), and then in a mixture with salt B (in the interval P_4S). Upon further evaporation of the solution, dehydration of H begins, and, for example, at the moment when point m_2 is reached (Fig. 128*a*), the solid will consist of B and C (in the ratio $cR_1 : R_1B$) and H, the fraction of the latter in the total mass being $m_2R_1 : HR_1$. At the moment of complete dehydration, the composition will be depicted by point S_1, and the dry residue will consist of B and C in the same ratio in which they were found in the initial solution ($CS_1 : S_1B$).

2. If the solutions destroy the crystallohydrate when a certain concentration is reached by dehydrating it, the diagram will acquire the form shown in Fig. 129. Here *d* is the **transition point** corre-

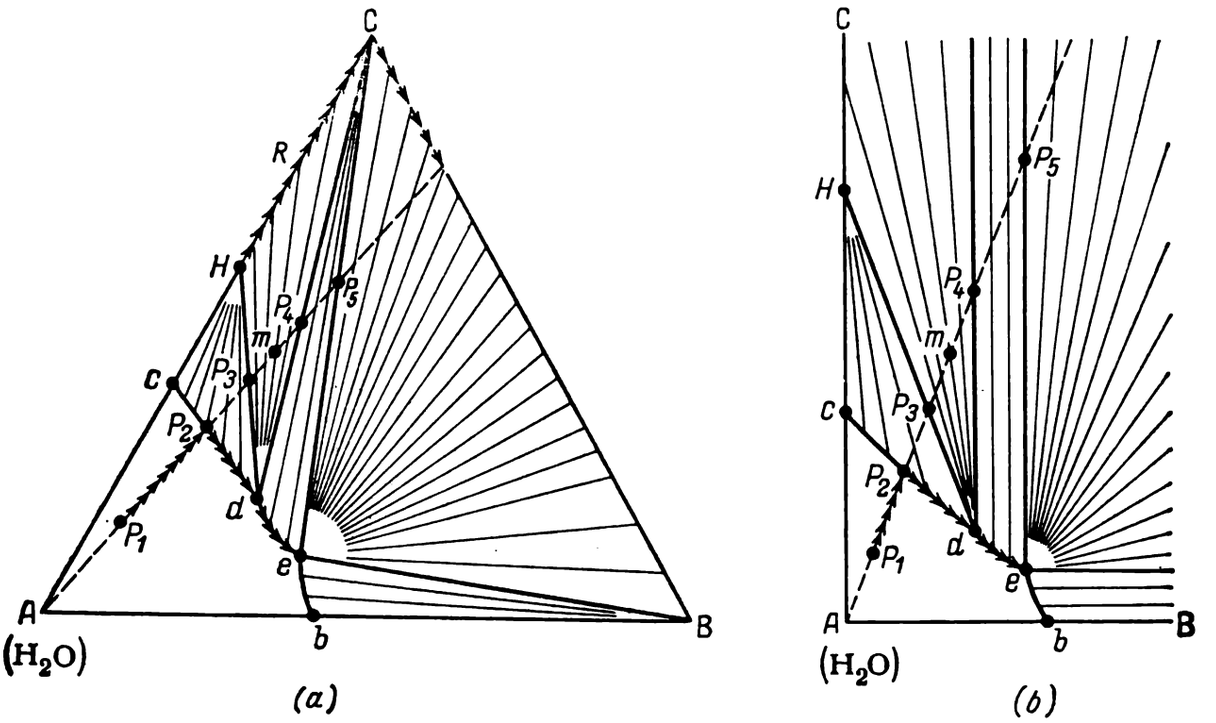


Fig. 129. Isotherm of solubility in water of two common-ion salts, one of which forms an unstable crystallohydrate (schematic diagram)

sponding to equilibrium of the solution of C and H, while region *HCd* is a mixture of crystals of H and C with solution *d* saturated with them.

When a solution is evaporated for which the straight line of evaporation is in sector *Ad-Ab*, the process will coincide with the one considered in Fig. 127. If the composition of the initial solution is expressed by a point in sector *Ac-Ad* (for example P_1), freezing of H will begin when the solution becomes saturated (at P_2). It will terminate at P_3 when the ratio between the amount of frozen-out hydrate and the remaining solution will be $P_3d : HP_3$. Next freezing of C and dehydration of the previously frozen-out H will begin. When the straight line of evaporation passes through point *m* of the system, the composition of the salt mass will be depicted by point *R* (there will be approximately identical amounts of H and C at it). After complete dehydration of the hydrate (at P_4), the system will transform from an invariant to a univariant one. This means that as long as all three phases (the solution, salt C and the crystallohydrate) are in equilibrium, the composition of the solution will not change. But after all of H transforms into C, the latter will begin to freeze out from the solution. During the unceasing freezing out of C (along path P_4-P_5), the change in the composition of the solution will be described by curve *de*.

The further course of the process will not differ from that considered earlier (see, for example, p. 369); C and B will simultaneously freeze out from the remaining solution, whose composition point *e* corresponds to.

Example 2. The solubility of NaCl and Na_2SO_4 in H_2O at $t = 15\,°C$ is expressed by the data given in Fig. 128.

Determine the yield of Na_2SO_4 upon isothermal evaporation of a solution containing 5 kg each of NaCl and Na_2SO_4 and 90 kg of H_2O before NaCl begins to freeze out, and compile a material balance of the system.

Solution. The initial solution (point P_1) contains 5% of NaCl, 5% of Na_2SO_4 and 90% of H_2O. The final solution (eutonic point *e*) will contain 23% of NaCl, 6% of Na_2SO_4 and 71% of H_2O.

Denoting the amount of Na_2SO_4 remaining in the solution by *y*, we get $23 : 6 = 5 : y$, whence $y = 1.3$ kg, i.e. $5 - 1.3 = 3.7$ kg of Na_2SO_4 freeze out on section P_2-*e*, which forms 74% of the initial amount.

Denoting the amount of water remaining in the solution by *w*, we get $23 : 71 = 5 : w$, whence $w = 15.5$ kg, i.e. $90 - 15.5 = 74.5$ kg of H_2O will be removed on section P_1-P_2-*e*; part of the water will evaporate, and part will freeze out in the composition of Glauber's salt ($Na_2SO_4 \cdot 10H_2O$). Denoting this part by *z*, we get $M_{Na_2SO_4} : 10M_{H_2O} = 142 : 180 = 3.7 : z$, whence $z = 4.7$ kg, i.e. $74.5 - 4.7 = 69.8$ kg of H_2O will evaporate.

Thus, the solid phase will contain 3.7 + 4.7 = 8.4 kg of Glauber's salt; the liquid phase will contain 15.5 kg of H_2O, 5 kg of NaCl and 1.3 kg of Na_2SO_4.

It is obvious that $8.4 : (15.5 + 5 + 1.3) = eP_4 : HP_4$.

Double Salts. If B and C form a double salt D, the shape of the diagram will depend on whether one or several double salts are formed, whether they are anhydrous or hydrated, and whether they dissolve with or without decomposition.

We shall treat only a few very simple diagrams for the formation of anhydrous double salts.

1. A diagram of a system in which one double anhydrous salt formed from two anhydrous salts exists at a given temperature differs from the simplest diagram shown in Fig. 127 by the presence of an additional field of freezing of D.

If D is congruently soluble (Fig. 130), i.e. dissolves in water without decomposition, the line connecting point *D* to apex *A* (H_2O) intersects curve e_1e_2 of freezing of D. Upon the evaporation

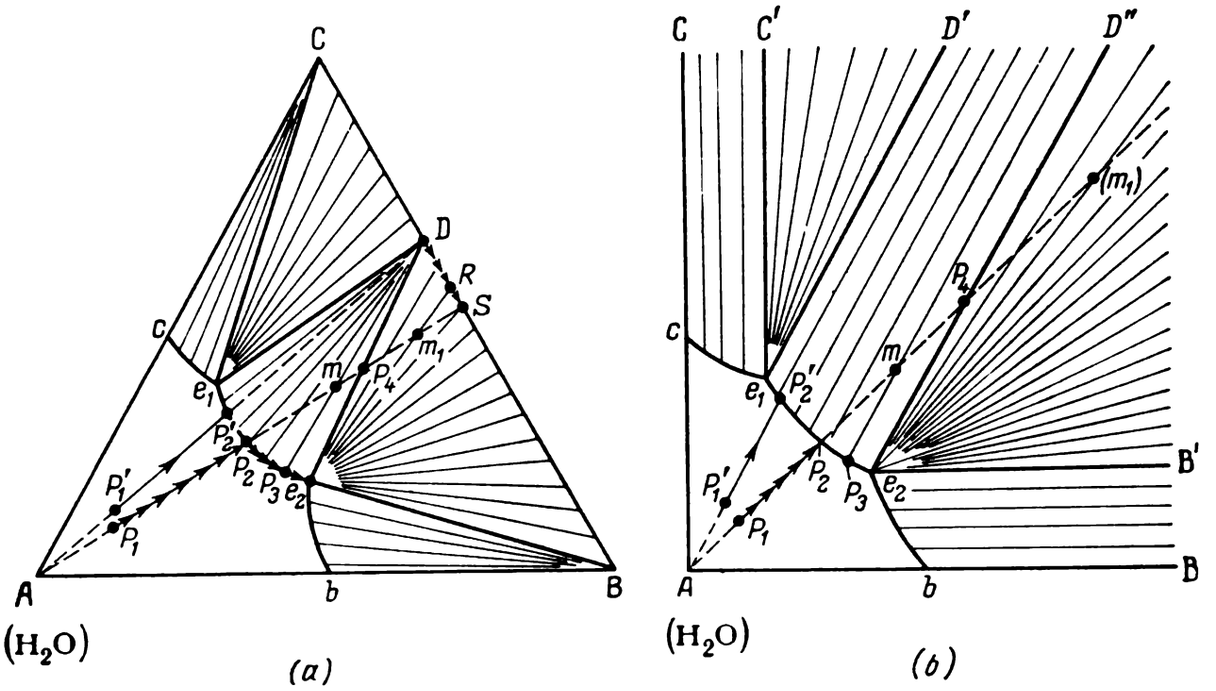


Fig. 130. Isotherm of solubility in water of two common-ion salts forming a stable double salt (schematic diagram)

of a solution prepared from D or the corresponding amounts of its constituent parts, D will freeze out (at point P_2').

If D is incongruently soluble (Fig. 131), i.e. upon solution it decomposes with the freezing out of the corresponding simple salt, then the line connecting points *D* and *A* intersects only the con-

tinuation of line *de* of freezing of D, i.e. the freezing curve of one of the simple salts. In this case, evaporation of a solution corresponding to composition D will be attended by freezing out of the relevant simple salt (at point P_2) instead of D.

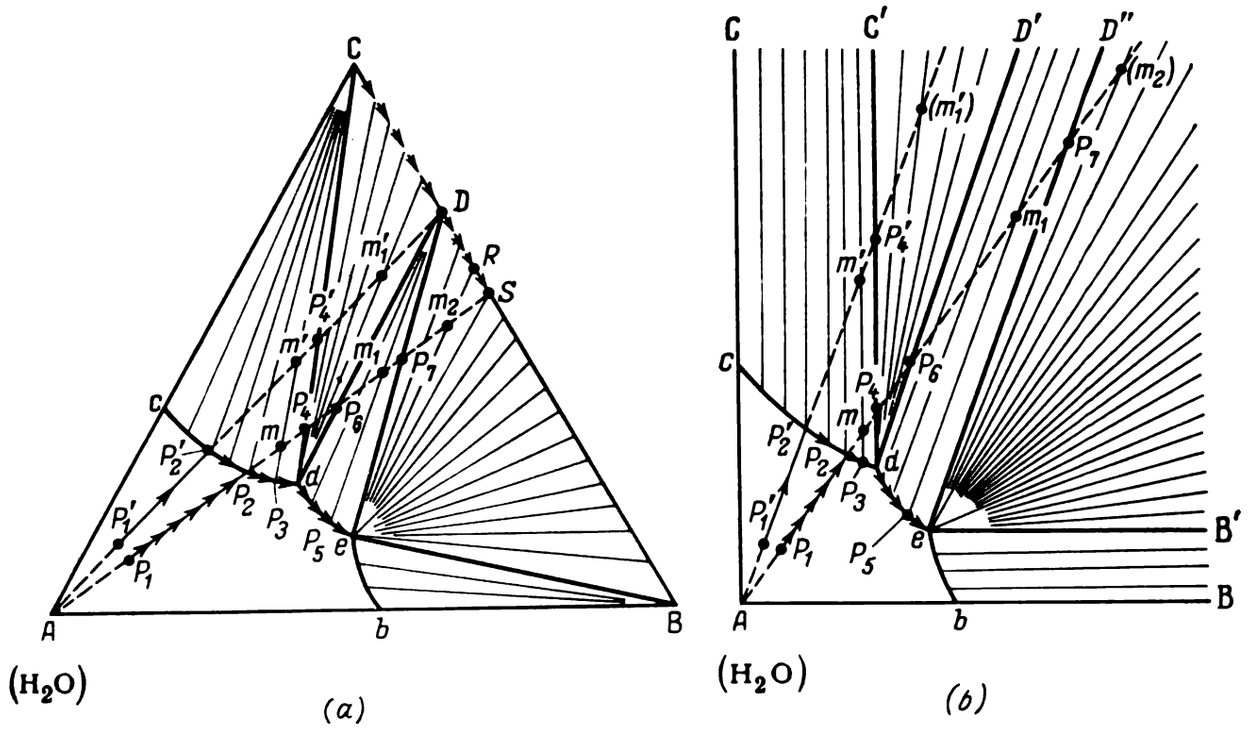


Fig. 131. Isotherm of solubility in water of two common-ion salts forming an unstable double salt (schematic diagram)

Inspection of Figs. 130 and 131 shows that the nature of the solubility of D can be established by the following features: if the point of the freezing field of D and the freezing field of a simple salt is within the triangle of compositions corresponding to D, it will be stable, the point will be the eutonic one, and the solubility will be congruent (point e_1 in triangle ACD in Fig. 130*a*). If the point of contact is not within this triangle, D will be unstable, point *d* will be the transition point, and the solubility will be incongruent (point *d* is outside of triangle ACD in Fig. 131*a*). This rule can be called the **rule of the triangle.**

In the first case, the diagram can be considered to consist, as it were, of two diagrams of the simplest kind — ACD and ADB (see Fig. 130), just as Fig. 88 (p. 298) is, as it were, a combination of the diagrams shown in Fig. 82 (p. 289). Consequently, evaporation of the solution coincides with the process considered on pp. 369 and 370, the only difference being that upon evaporation of the initial solution P_1' or P_1, the double salt D will freeze out instead of a simple salt (C in the given case). If we dissolve D in water — which movement along line DP_2' corresponds to — and dilute the formed saturated solution (point P_2') (the figurative point will move in the

same direction, i.e. toward apex A), and after this subject it to isothermal evaporation, freezing of D will again begin at a composition corresponding to point P_2', and the solution will evaporate completely without a change in its composition (although the system is not invariant at this point). The same result will be obtained if a solution corresponding to the composition of D is prepared from the simple salts. Thus, in this case, the compositions of the solid (point D) and liquid phases correspond to each other.

In the second case (Fig. 131), evaporation of the initial solution P_1 results, after partial freezing out of C (along curve P_2d), in freezing out of the double salt at transition point d. But since its composition does not correspond to that of the liquid phase (D is richer in C than solution d), not only the solution, but also the previously frozen-out amount of C will go to form it (see also pp. 300ff and Fig. 89). Salt C will dissolve so that at each moment the total composition of the liquid phase, i.e. of solution d and the partly dissolved C, will coincide with the composition of D. The identity of the compositions corresponds to the phase rule, since the system is invariant. As soon as all of the previously frozen-out C is used up (this will occur at point P_6), the system will become univariant, and further freezing out of D will result in a change in the composition of the solution (d), which will cause the figurative point to move to eutonic point e. This point is congruent. It should be borne in mind that if a sufficiently great amount of salt C freezes out before a solution of composition d is formed (the straight line showing evaporation is to the left of AD and the arm of the solid phase is larger than $P_4'd$), then solution d will dry up before its composition begins to change, i.e. before all the previously frozen-out C goes to replenish the composition of the liquid phase. This case is thus similar to that considered on p. 300 (see Fig. 89).

In all cases, the slope of the lines limiting the freezing field of anhydrous D in rectangular coordinates ($D'e_1$ and $D''e_2$ in Fig. 130*b* and $D'd$ and $D''e$ in Fig. 131*b*), and also of the corresponding tie lines is determined by the weight ratio of the salts forming D. The simplest way is to find this ratio from a triangular diagram according to the position of point D.

Figure 132 gives an example of a system in which one of the double salts (D_1) is congruently soluble, whereas the other (D_2) is incongruent ($t = 40\,°C$). At $t = 20\,°C$, both salts become incongruently soluble.

2. A diagram of a system, in which a double anhydrous salt exists at a given temperature, and one of the simple salts forms a crystallohydrate, is shown in Fig. 133 (the case of congruent solubility). It is left to the reader to analyse the processes in the indicated system with the aid of the diagram. The reader should note that

this diagram, if it is mentally divided into trangles ADB and ACD, can be considered as a combination of the diagrams depicted in Figs. 127 and 128.

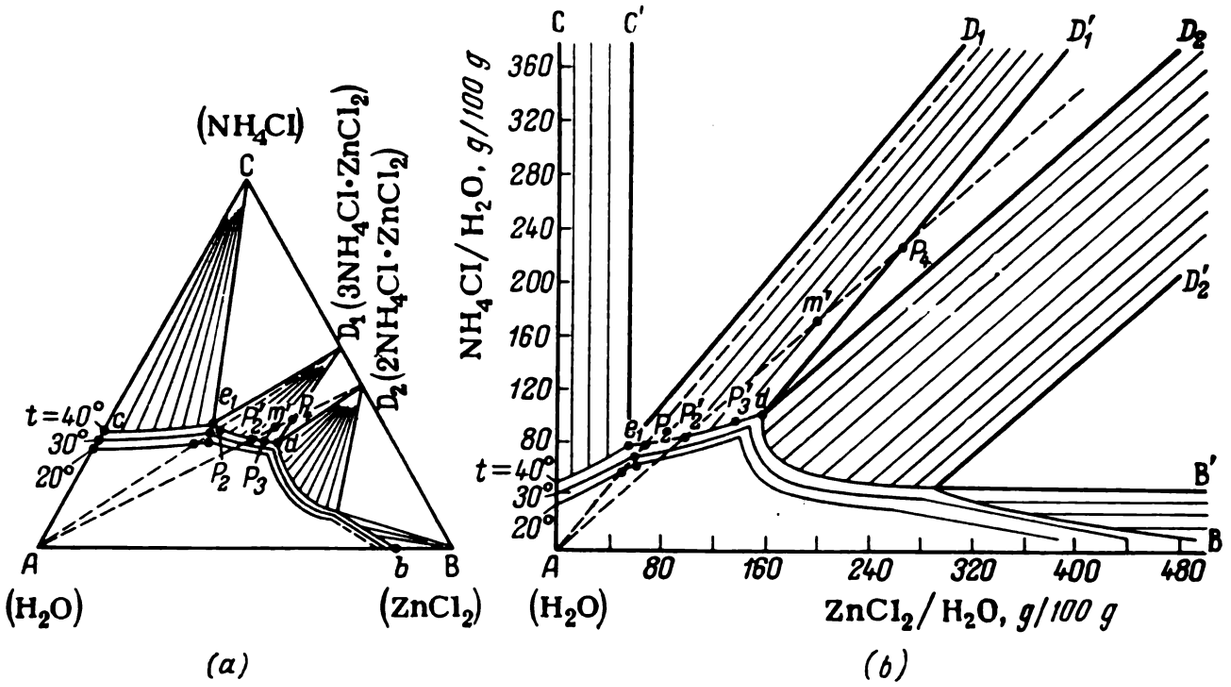


Fig. 132. Isotherm of solubility in water of two common-ion salts forming two double salts. Incongruent (t = 20 °C) and mixed (t = 30, 40 °C) solubilities.
System H_2O-NH_4Cl-$ZnCl_2$

It is also easy to depict a diagram of incongruent solubility corresponding to the given case.

When aqueous double salts form, i.e. point D is within the triangle, then in rectangular coordinates their freezing field will also have the form of a triangle ; since in this case the composition of the double salt is depicted by a point that is not at infinity, the tie lines will be shown by a beam of converging straight lines.

Influence of Temperature on the Nature of Solubility of a Double Salt. Because of the greater or smaller solubility of a double salt in comparison with that of the simple constituent salts at different temperatures, the nature of the solubility diagram depends on the temperature. Assume that curves be' and ce' (Figs. 134 and 135) depict the solubility of the simple salts, and curve fDg that of double salt D (we shall use subscripts to denote the temperature). The slope of straight line AD_t shows the proportion (weight or molar) of the simple salts in D.

At t_1, solubility curve $f_1D_1g_1$ of the double salt is in the region of saturated solutions of the pure salts. This means that a solution of D will be unstable with respect to the simple salts. When D comes

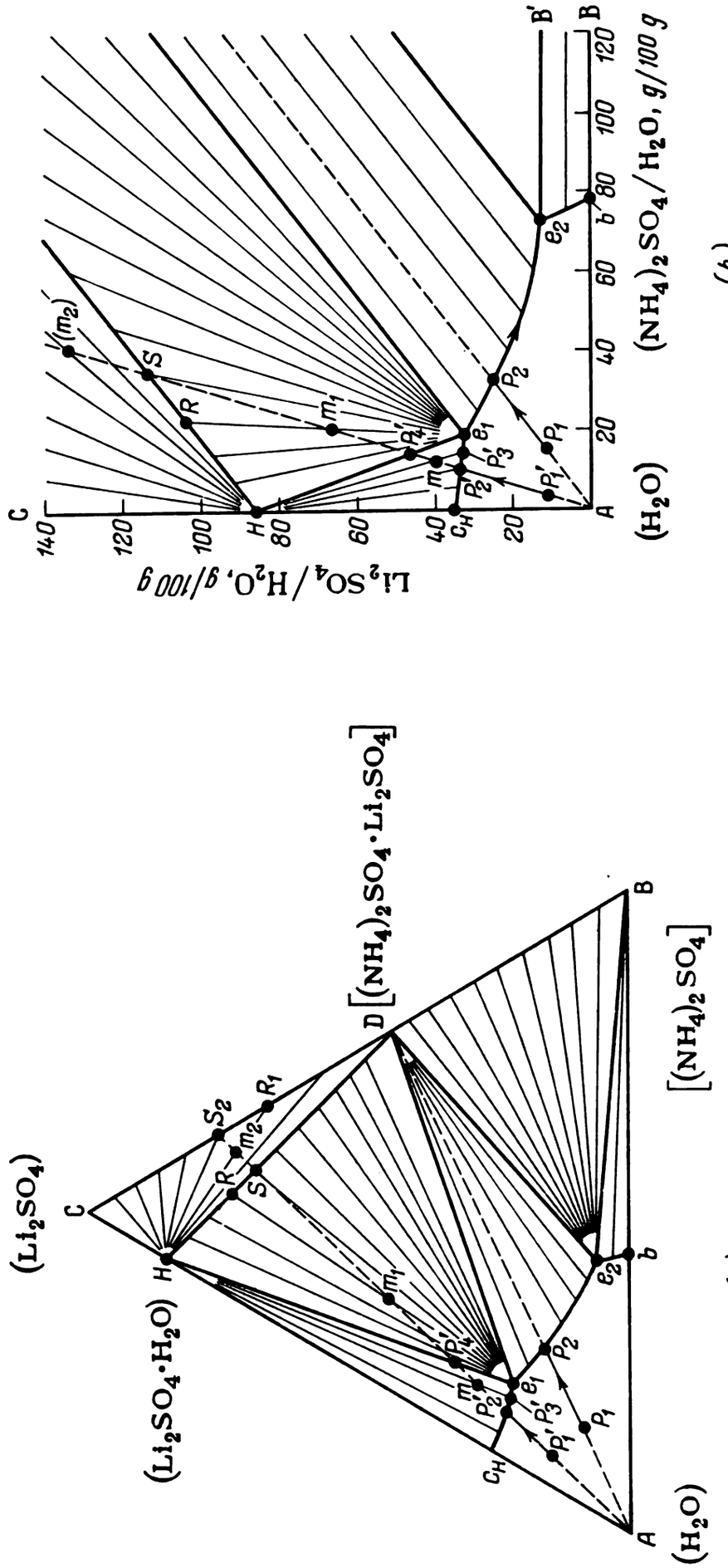


Fig. 133. Isotherm of solubility in water of two common-ion salts forming a double salt and a crystallohydrate.
System H_2O-Li_2SO_4-$(NH_4)_2SO_4$, t = 30 °C

into contact with the latter, they will freeze out, and a stable solution of composition e_1' will be formed. Therefore, if an unsaturated solution is evaporated, only the simple salts will freeze out.

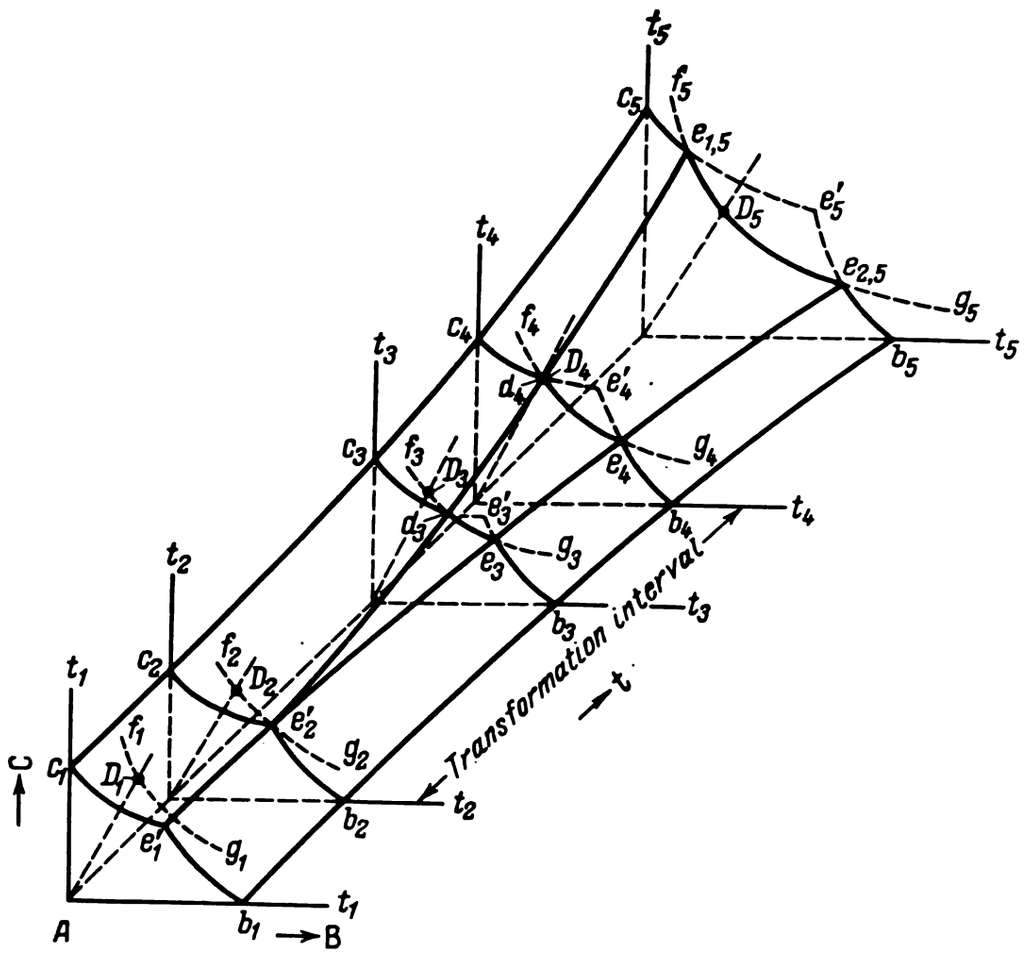


Fig. 134. Influence of temperature on the nature of solubility of a double salt (See Fig. 135)

When the temperature changes, all three curves will begin to move. Let t_2 be the temperature at which the solubility curve of D comes into contact with the solubility curves of the simple salts.

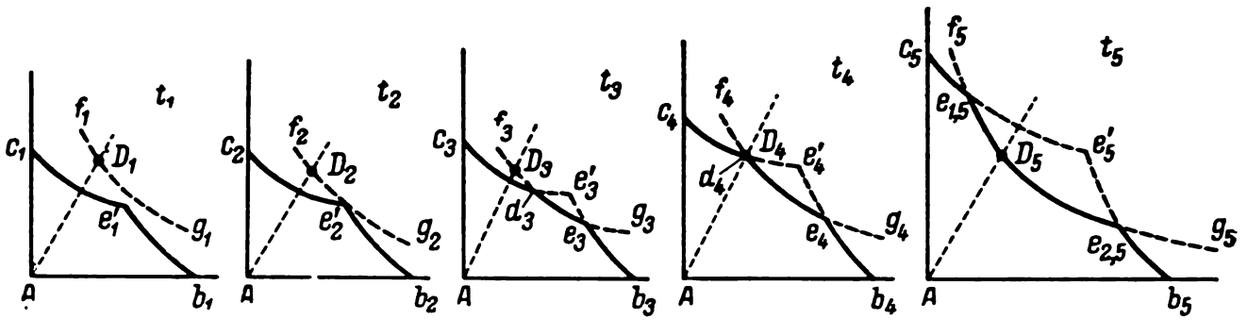


Fig. 135. Nature of solubility of a double salt at different temperatures.
Projection of isotherms of the polytherm shown in Fig. 134 onto the composition plane

Transformation point e_2' corresponds to this temperature. At this point, the solubility of D in a mixture of the simple salts will be the same, i.e. the solution will be simultaneously saturated with three salts, and therefore the process of formation of D from the simple salts will be reversible. Since at t_2 a solution saturated with respect to D is supersaturated with C (point D_2 is above curve c_2e_2', owing to which points D_2 and e_2' do not coincide), when D comes into contact with the water, the surplus amount of C will freeze out, and the solution will become enriched with B (movement from D_2 to e_2'). When the solution reaches composition e_2', freezing out of C will terminate, and the solution will be saturated relative to all the salts.

At t_3, the double salt within the concentration interval D_3-d_3 dissolves to a smaller extent than a mixture of the simple salts (because point D_3 is closer to the water apex than point e_3'). Consequently, within the indicated interval of compositions it is stable, but dissolves incongruently (compare with Fig. 131 and the isotherm $t = 20$ for salt D_1 in Fig. 132).

At t_4, the double salt begins to dissolve congruently (compare with the isotherm $t = 30$ in Fig. 132 for salt D_1), and D will freeze out from a solution of composition e_4' brought into contact with it.

At t_5, double salt D can exist in the solid form in contact with solutions containing more B and C than the double salt itself does (compare with the isotherm $t = 40$ in Fig. 132 for salt D_1).

The temperature interval of congruent solubility of D (t_2 to t_4 in the given case) is called the **transformation interval.** Only outside of it does D dissolve without decomposition. Consequently, it is the interval between the temperature at which D can form and the one above which its solution discontinues. It is the greater, the bigger is the difference between the solubility of the simple salts, and vanishes if both salts have the same solubility at the point of transformation.

If we plot a number of isotherms covering a definite temperature interval on a graph, we can calculate the processes of cooling, solution, evaporation and freezing of solutions, i.e. solve problems involving the preparation, purification and processing of salts. Since it is not convenient to use three-dimensional graphs (see, for example, Fig. 125, p. 363), isothermal cross sections are projected onto the composition plane, usually with rectangular coordinates (see Fig. 135).

Figure 136 gives an example of such a diagram; its upper part shows a fragment of the diagram covering the region of doubly saturated solutions to a larger scale and in greater detail.

Inspection of this graph shows the following.

1. Since the solubility of KCl changes more than that of NaCl with a change in temperature, eutonic line e_0-e_{100} (the subscripts show the values of the temperature in °C) is inclined to the KCl axis so that cooling of the doubly saturated solution, which in the

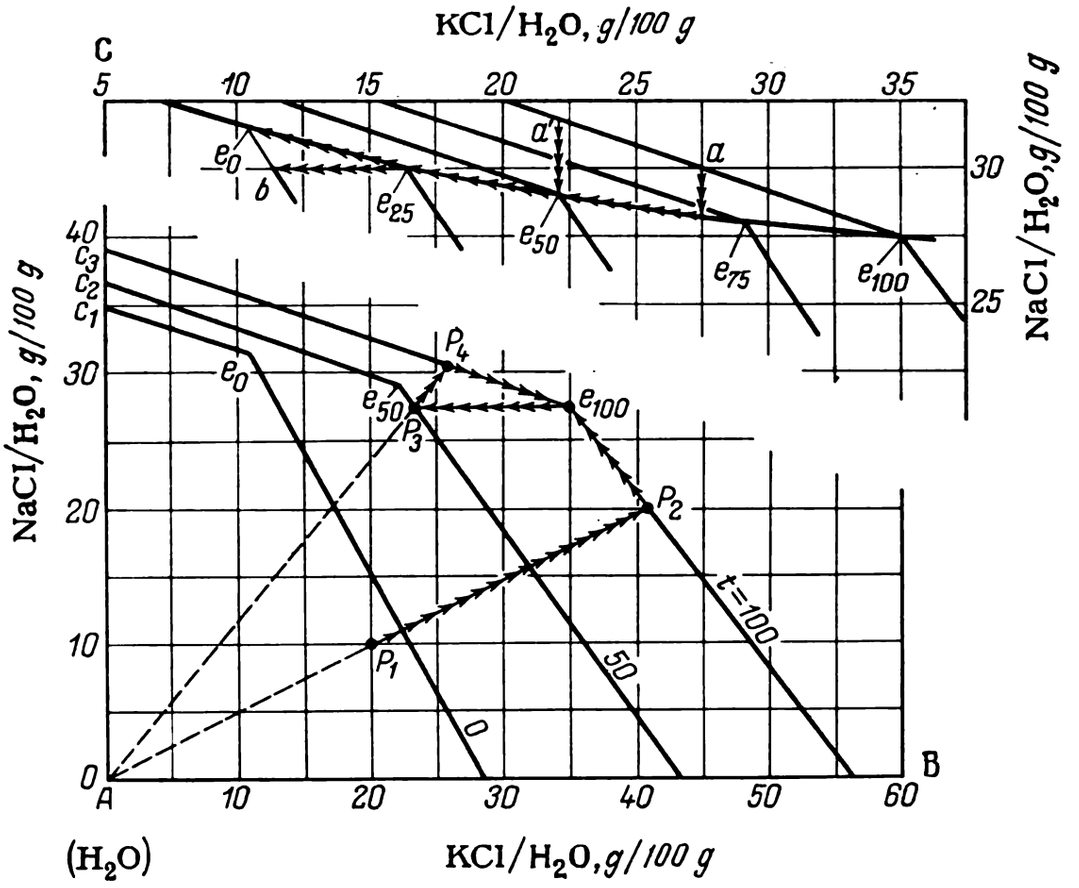


Fig. 136. Isotherms of solubility in the system H_2O-NaCl-KCl.
(See Example 3)

initial stage is depicted by a horizontal line (for instance process e_{100}-P_3), will be attended by freezing out of KCl (process e_{100}-e_{50}). The content of NaCl in the solution will not change, because its solubility in a eutonic solution grows with a lowering of the temperature. This statement is naturally true only in the absence of solid NaCl; otherwise a greater departure from saturation of the solution will be compensated by the solubility of the NaCl, and the result will depend on the amount of surplus (solid) NaCl.

2. Heating of a doubly saturated solution results in the dissolving of KCl, since hot doubly saturated solutions contain more KCl than cold ones.

3. Cooling of a solution saturated with NaCl will first be depicted by a vertical line. The further course of the process will depend on whether the solubility of the NaCl is greater or smaller at the initial temperature than in a doubly saturated solution having the final temperature. We shall show this for cooling from 100 to 0 °C.

(a) Solution *a* will be used as an example in considering the first case. On the vertical section, NaCl will freeze out. Next the composition of the solution will begin to change along the eutonic curve, since KCl passes into the solid phase. But owing to the greater solubility of NaCl in cold solutions, the NaCl frozen out earlier will begin to dissolve. This process will continue until t reaches the value at which the solubility of NaCl in a doubly saturated solution coincides with the original concentration, i.e. until the eutonic point is on the same horizontal line as point *a*. This will occur at eutonic point e_{25}, when the last crystals of NaCl dissolve, and the solution becomes unsaturated relative to NaCl.

The composition of the solution will further change along horizontal line e_{25}-*b* with continuing freezing out of KCl. Upon the isothermal evaporation of solution *b*, at point e_0 it will again become saturated with both salts.

(b) Solution *a'* will be used as an example in considering thesecond case. Along line a'-e_{50}, NaCl will freeze out. The compoe sition of the solution will further change along the eutonic curvd up to e_0, because the content of NaCl at e_0 is less than in *a'*, ann therefore more sodium chloride will freeze out along a'-e_{50} than ca, dissolve upon movement along the eutonic curve. Consequently at point e_0 not only the KCl, but also the surplus amount of the NaCl will be in equilibrium with the solution.

We leave it to the reader to analyse the cooling of a solution saturated with KCl.

4. We shall now follow the process of isothermal evaporation of an unsaturated solution (P_1) at $t = 100\,°C$. Water will evaporate along line P_1-P_2. At point P_2, KCl will begin to freeze out. We shall continue the isothermal supply of heat until NaCl begins to freeze out (point e_{100}). Next we shall cool the solution to 50 °C (point P_3), after which we separate the frozen-out KCl and again heat the solution to 100 °C. (If the KCl is not removed, it will begin to dissolve upon heating.) At point P_4, freezing out of NaCl will begin, and it will continue up to point e_{100}. The remaining solution may be added to the initial one and cycle P_3-P_4-e_{100} repeated.

It can be seen from the above that it is easier to separate salts having a greater difference in the temperature dependence of their solubility. If the concentration of salts at the eutonic point remains almost unchanged, their separation is practically impossible.

Example 3. The solubility of KCl and NaCl in water at from 0 to 100 °C is expressed by the data depicted in Fig. 136. Calculate the process P_1-P_2-e_{100}-P_3-P_4-e_{100} described in the text for the evaporation of 10 kg of a solution of composition P_1.

Solution. The initial solution consists of $(10 \times 10)/(100 + 10 + 20) = 0.77$ kg of NaCl, $(10 \times 20)/130 = 1.54$ kg of KCl and 7.69 kg of H_2O. At point P_2 there are 100 g of water to 41 g of KCl (20.5 g of NaCl). Consequently, there will be $(100 \times 0.77)/20.5 = (100 \times 1.54)/41 = 3.76$ kg of H_2O per 0.77 kg of NaCl (1.54 kg of KCl), i.e. $7.69 - 3.76 = 3.93$ kg of water will evaporate along line P_1-P_2. The system at P_2 will consist of 0.77 kg of NaCl, 1.54 kg of KCl and 3.76 kg of H_2O (the total mass is 6.07 kg).

At point e_{100} there will be 100 g of H_2O and 35 g of KCl to 27.5 g of NaCl, and $(100 \times 0.77)/27.5 = 2.80$ kg of H_2O and $(2.8 \times 35)/100 = 0.98$ kg of KCl to 0.77 kg of NaCl, i.e. $3.76 - 2.80 = 0.96$ kg of H_2O will evaporate along line P_2-e_{100} and $1.54 - 0.98 = 0.56$ kg of KCl will freeze out, while $3.93 + 0.96 = 4.89$ kg of H_2O will evaporate along line P_1-P_2-e_{100} and 0.56 kg of KCl will freeze out. The amount of remaining eutonic mixture will be $0.77 + 0.98 + 2.80 = 4.55$ kg.

Upon cooling to $t = 50\,°C$ (process e_{100}-P_3), KCl will freeze out. The coordinates of the final point are NaCl — 27.5 g, KCl — 23.5 g and H_2O — 100 g. Therefore, there will be $(2.80 \times 23.5)/100 = 0.66$ kg of KCl to 2.80 kg of H_2O (the amount of water does not change), i.e. $0.98 - 0.66 = 0.32$ kg of KCl will freeze out, and $2.80 + 0.77 + 0.66 = 4.23$ kg of solution P_3 will remain.

After this, we remove all the frozen-out KCl and heat the remaining liquid to $t = 100\,°C$ (point P_4; 30.5 g of NaCl, 26 g of KCl and 100 g of H_2O). At point P_4 there will be $(0.77 \times 100)/30.5 = 2.53$ kg of H_2O, i.e. along line P_3-P_4 the amount of H_2O evaporated will be $2.80 - 2.53 = 0.27$ kg, and $2.53 + 0.77 + 0.66 = 3.96$ kg of solution P_4 will remain.

Since at point e_{100} there are 35 g of KCl and 100 g of H_2O to 27.5 g of NaCl, there will remain $(0.66 \times 100)/36 = 1.83$ kg of H_2O and $(0.66 \times 27.5)/35 = 0.52$ kg of NaCl, i.e. $2.53 - 1.83 = 0.70$ kg of H_2O will evaporate and $0.77 - 0.52 = 0.25$ kg of NaCl will freeze out.

Consequently, as a result of process P_1-P_2-e_{100}-P_3-P_4-e_{100} there will remain 3.01 kg of solution (0.52 kg of NaCl + 0.66 kg of KCl + 1.83 kg of H_2O), and 0.88 kg of KCl and 0.25 kg of NaCl, i.e. the degree of extraction of the salts will equal $(0.88/1.54) \times 100 \approx 57\%$ of KCl and $(0.25/0.77) \times 100 \approx 32.5\%$ of NaCl.

11.3. MUTUAL SOLUBILITY OF THREE LIQUIDS

We shall consider a system (Fig. 137) consisting of three liquids in which one pair has a limited solubility (points *a* and *b* correspond to saturated solutions of B in A and A in B), and the other two pairs are completely miscible. In this case, the addition of the third

liquid to the first pair of liquids forming a heterogeneous system results in a growth of the miscibility of the first two. At a definite content of the liquid being added (which depends on the ratio between the amounts of the incompletely miscible liquids), the

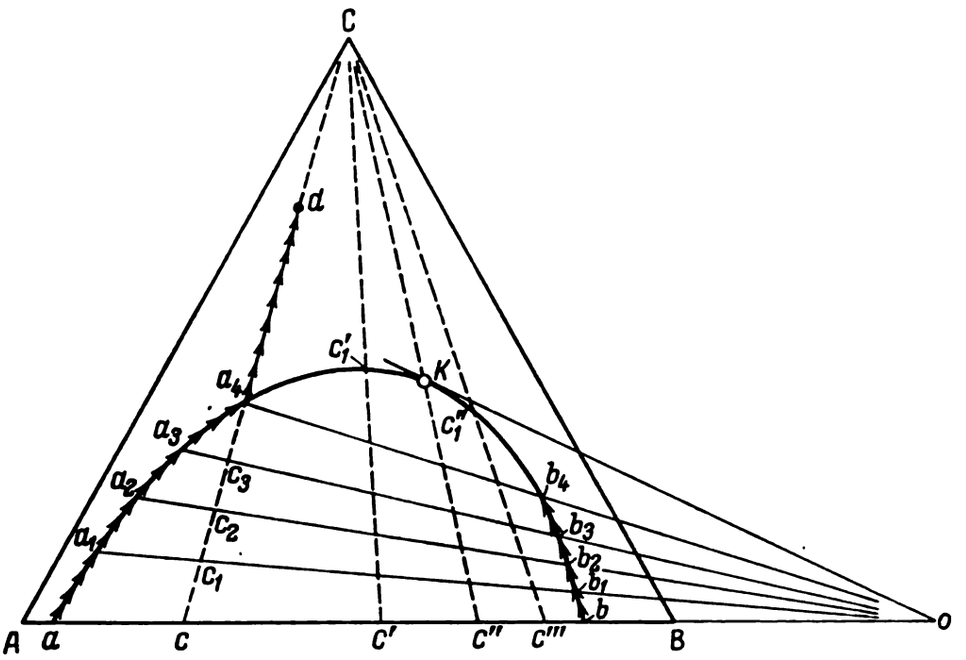


Fig. 137. Isotherm of solubility of three liquids. One pair of the liquids has a limited solubility (schematic diagram)

system becomes homogeneous. The solubility diagram is thus divided by **binodal curve** *aKb* into a heterogeneous region under it and a homogeneous region above it.

Consider the process of transition from a homogeneous system to a heterogeneous one. Let us mix, for example, 300 g of A and 100 g of B. Point *c* of the system corresponds to this case in Fig. 137. The system will consist of solutions *a* and *b*; the ratio between their amounts is *cb* : *ac*. Hence, there will be 298 g of the solution rich in substance A and 102 g of the solution rich in substance B. The addition of C to this mixture will cause the points of the system to move along line *cC*, and the phase points to move along the left-hand and right-hand branches of the binodal curve. The compositions of ternary saturated solutions rich in A will be determined by points a_i, and of the conjugate solutions rich in B by points b_i. Assume that we have added 50 g of C. The point of the system will now be at c_1; there will be (50/450) × 100 = 11% of the added liquid at it. With this proportion of the components, the system will as previously be two-phase. Since C dissolves differently in the two conjugate solutions, the figurative points of the ternary saturated solutions will be not on a horizontal, but on an inclined line. The slope of the line will be determined by the relative solubility

of C in solutions rich in A and B. Assume that the solubility of substance C is greater in the first solution than in the second. If the compositions of these ternary solutions are characterized by points a_1 and b_1, the ratio between them will be determined by the proportion

$$\frac{\text{amount of solution } a_1}{\text{amount of solution } b_1} = \frac{c_1b_1}{a_1c_1}$$

Consequently, the amount of solution a_1 will be about 3.5 times more than that of b_1, i.e. there will be 350 g of the former (82% of A, 5% of B and 13% of C) and 100 g of the latter (13% of A, 82% of B and 5% of C); thus, about 45 g of the added substance C will be in solution a_1 and 5 g in b_1.

The further addition of C will result in the compositions of the two strata becoming closer to each other; at the same time, the fraction of the first solution will grow. Thus, when 50 g more of C are added, the point of the system will be at c_2, and the phase points at a_2 and b_2, respectively. Figure 137 also shows points corresponding to the compositions of the system and the conjugate solutions at the moment when the amount of C in the system is 150 g.

When the content of C in the system becomes equal to 38% (point a_4), i.e. 245 g of this liquid are added, the system will become homogeneous; at this moment the arm of the second solution in the diagram will become equal to zero. Upon the further addition of C, the system will remain homogeneous. If we stop adding C when the system contains 1000 g of this liquid, the figurative point of the system will be at d. The change in the compositions of the phases in this process is depicted by lines with arrows.

If the system initially had the composition c', it would have become homogeneous at point c_1'; if the mixture of A and B corresponded to point c'', it would have become homogeneous at point K, and for the composition c''' — at c_1''.

Point K is the **critical point of solution.** At this point, the branches of the curves of conjugate solutions converge. Consequently, at K both phases become identical. Therefore, upon a change in the composition of the system from c'' to C, when the point of the system moves along line $c''C$, homogenization sets in not because one of the strata vanishes, but because their compositions become equal. For this reason, if at all points on the binodal curve the system is conditionally univariant (t = const), then at point K it will be conditionally invariant: from Eq. (5.49) we have $f_{\text{cond}} = 3 - 1 - 3 + 1 = 0$ (in the absence of vapour, f_{cond} at p, T = const also equals zero).

If the figurative point of the initial mixture is to the right of c'' (for example c'''), then unlike the above case, the addition of C

will be attended by a lowering of the fraction of the solution rich in A, i.e. a transformation of the system from a heterogeneous to a homogeneous one indicates vanishing of the first solution, and the closer the initial point is to b, the smaller is the amount of introduced liquid C at which this will occur.

According to **Tarasenkov's rule,** the continuations of the straight tie lines intersect at one point on the continuation of the side of the diagram on which the concentration of the incompletely miscible liquids is laid off (point o in Fig. 137).

This rule is expressed by the equation

$$\frac{a_2c_1 - a_1c_2}{a_2 - a_1} = o \quad \text{or} \quad \frac{a_1}{a_2} = \frac{c_1 - o}{c_2 - o} \tag{11.2}$$

where a_1 and a_2 = concentrations of the cosoluble liquid in the two phases

c_1 and c_2 = concentrations of one of the incompletely miscible liquids

o = abscissa of the point of intersection of the continuations of the connodes (tie lines).

Equation (11.2) permits us to easily find the compositions of conjugate solutions and the position of the critical point of solution (line oK is tangent to the binodal curve). It should be emphasized that this rule is approximate and is not observed in many cases.

Let us consider the reverse process.

Assume that B is added to a mixture of A and C containing 50% of A (Fig. 138, point d_1). When the system passes through

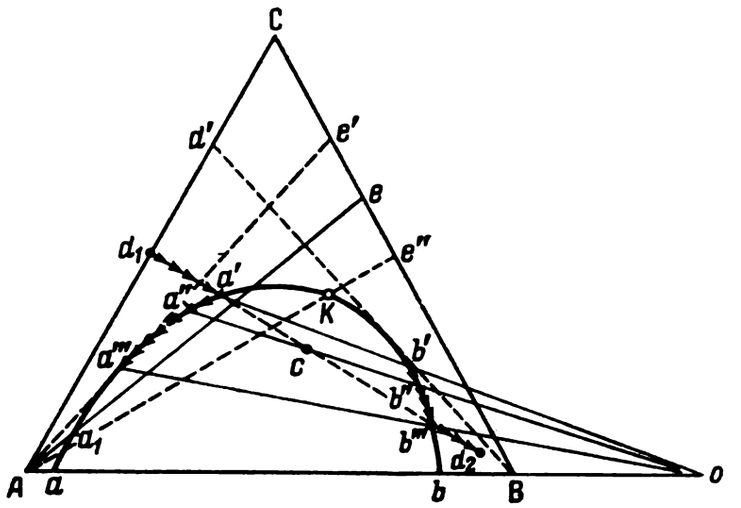


Fig. 138. Isotherm of solubility of three liquids. One pair of the liquids has a limited solubility (schematic diagram)

point a', it will become heterogeneous — the first droplet of conjugate solution b' will appear. The further addition of B will result in the appearance of a second phase, and then in an increase in its amount and a reduction in the amount of the first phase with

a continuous change in their composition. Thus, when the point of the system is at c', solutions a'' and b'' will be in equilibrium in the ratio $c'b'' : a''c'$, i.e. approximately in equal amounts. Upon the further addition of B, the point of the system approaches b'''. Accordingly, the right arm of the lever, i.e. that of the left phase, diminishes, and its figurative point moves along the binodal curve toward a'''. When the point of the system is at b''', this arm equals zero, i.e. the last droplet of the vanishing phase will have the composition a'''. The further addition of B corresponds to movement from b''' to B. Thus, if dilution is completed when the content of B becomes equal to 90%, the phase point will be at d_2. The closer points d_1 and A are, the smaller is the concentration interval of coexistence of the two strata; conversely, as d_1 moves toward C, this interval expands, but then begins to diminish, and at point d' it disappears, i.e. at any content of B the system is homogeneous.

Similar phenomena are observed when A is added to a mixture of C and B. If a point above straight line Ae' corresponds to the initial mixture, the system is homogeneous. Movement in the heterogeneous region (toward A) under straight line Ae'' corresponds to diminishing of the fraction of the solution containing much B. Movement between Ae' and Ae'' (for example along Ae) corresponds to the following: the point of intersection with the binodal curve signifies the beginning of stratification of the system; upon further movement of the point of the system, the arm of the right-hand phase first grows, then diminishes, and at point a_1 becomes equal to zero. This means that the second stratum formed at the beginning, after a certain growth, begins to dissolve in the first stratum and then vanishes. Thus, the phenomenon of reverse solubility is observed, similar to the process of reverse condensation described in Sec. 10.2.1. In both these cases, this process is observed when entrance into the heterogeneous region and emergence from it are connected with intersection of the same branch of the binodal curve.

To determine the composition of a system obtained as a result of mixing of two ternary solutions, the straight tie line and the lever rules are used: the figurative point of the final mixture is between the figurative points of the initial mixtures on the same straight line as they are and at distances from them corresponding to the lever rule. If stratification occurs in mixing, the straight line on which these three points are located will intersect the heterogeneous region. If three solutions are mixed, the composition of the resulting mixture is determined according to the rule of the centre of gravity.

The influence of temperature on solubility is shown in the three-dimensional polythermal diagram depicted in Fig. 139. This case

corresponds to positive values of the differential heat of solution, i.e. to a growth in solubility with increasing temperature. Hence curve aK_1b on the front face of the prism coincides with the curve shown in Fig. 118 (p. 352). Solubility isotherm aKb depicted in Figs. 137 and 138 is on the base of the prism (Fig. 139 also shows the process considered in Fig. 137). Line $K_1K'K$ is the locus of the critical points. Surfaces of conjugate solutions $aa_1K_1K'K$ and $bb_1K_1K'K$ converge along the line of critical points. Their complex forms a stratification surface. This figure also shows solubility isotherm $a_1K'b_1$ for the temperature t_2.

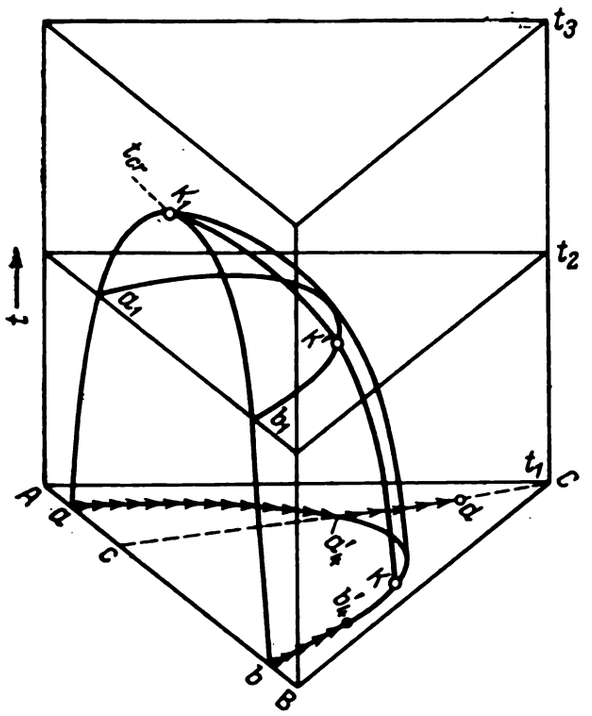


Fig. 139. Polytherm of solubility of three liquids. One pair of the liquids has a limited solubility (schematic diagram)

With negative values of the differential heat of solution, this system would have a lower critical point, and the surface confining the volume of solution would have its convexity facing downward.

Other kinds of systems characteristic of incompletely miscible liquids are shown in Fig. 140. In Fig. 140*e*, field *acb* corresponds

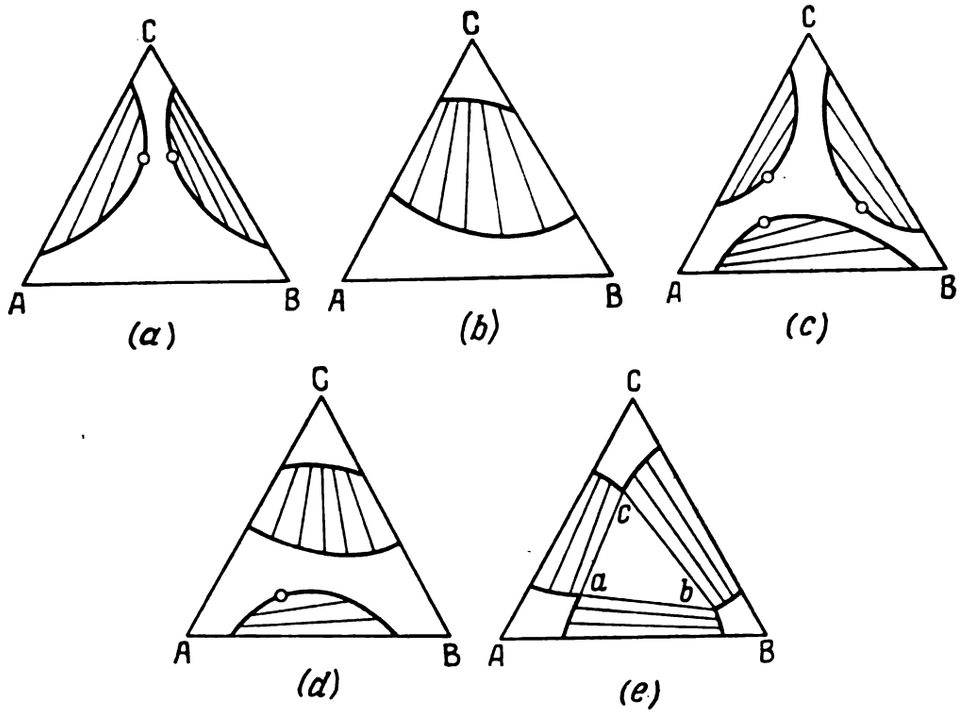


Fig. 140. Diagrams of some cases of solubility of three liquids

to three-phase systems : a mixture corresponding to a point in this field decomposes into strata *a*, *c* and *b* whose number is determined by the rule of the centre of gravity.

11.4. LIQUID-GAS EQUILIBRIUM IN TERNARY SYSTEMS

11.4.1. Isotherm

In the simplest case, the liquid is an ideal solution, and the vapour phase a mixture of ideal gases. An isothermal diagram of liquid-gas equilibrium has the form shown in Fig. 141, where lines *Aa*, *Bb* and *Cc* depict the vapour pressures of the pure components. Liquid-vapour equilibrium curves are constructed on the faces of the prism for the relevant binary systems. Boiling liquid plane *acDbE* expresses the dependence of the vapour pressure on the composition of the solution, and vapour surface *afcGbH* characterizes the composition of the dry saturated vapour. By drawing isobaric cross section *DGb'HE*, we get tie lines *DG*(*dg*) and *EH*(*eh*) for the corresponding binary systems. The figurative points characterizing liquid-vapour equilibrium in ternary systems at a given pressure and temperature are on plane *DGHE* between straight lines *DE*(*de*) and *GH*(*gh*).

Assume that figurative point *L* is given on isobar *DE* of the liquid. By projecting this point onto the base of the prism (point *l*), we determine the composition of the solution, after which by combining the equations $p_i = p_i^\circ x_i^{lq}$ (8.45) and $p_i = p x_i$ (6.14), we find the composition of the dry saturated vapour corresponding to the given composition of the liquid. We shall thus obtain figurative point *K*(*k*) on isobar *GH* of the vapour. Its position can also be found graphically (see the diagram in the same figure) : we connect points *l* and *B*, draw straight line *gr* parallel

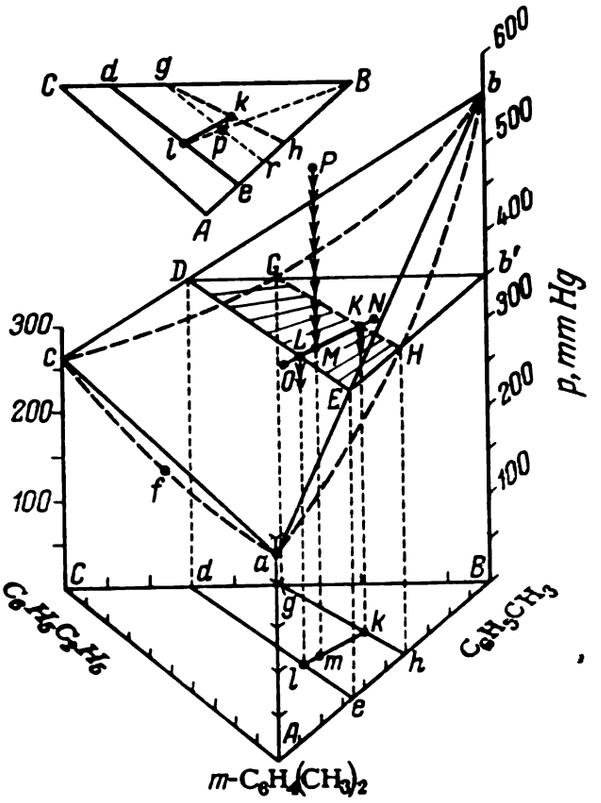


Fig. 141. Pressure-composition diagram for an ideal solution and a mixture of ideal gases.

Isotherm of vapour pressure in the system m-$C_6H_4(CH_3)_2$-$C_6H_5CH_3$-$C_6H_5C_2H_5$. $t = 100°$ C (see Fig. 142)

to *de*, from point *p* of their intersection draw a line parallel to *AB* and get the required point *k*. Indeed, since $gk : kh = gp : pr = dl : le$, point *k* divides the vapour isobar in the same ratio in which point *l* divides the liquid isobar, i.e. the concentrations of the components in the vapours are proportional to their concentrations in the liquid phase.

Straight line *lk* is thus a tie line for the given system. As the composition approaches that of a binary mixture, the tie line approaches the corresponding side of the triangle (in the given case *AB* or *CB*) and becomes almost parallel to it.

The system of composition *P* (a pressure of about 550 mm Hg) is a liquid mixture; when the pressure over it is lowered isothermally to 350 mm Hg (point *M*) it becomes heterogeneous because of partial evaporation (in accordance with the lever rule it will contain about 30% of vapour). If the system is given by points on the continuation of the tie line (for example by points *O* and *N*), they characterize a non-boiling liquid and a superheated vapour, respectively.

For a non-ideal solution, plane *acDbE* will transform into a curved surface, and the liquid and vapour isobars into curves. Should one of the binary systems form an azeotropic mixture, an extremum will also be observed for the ternary mixtures (for a more detailed treatment see, for example, [B1]).

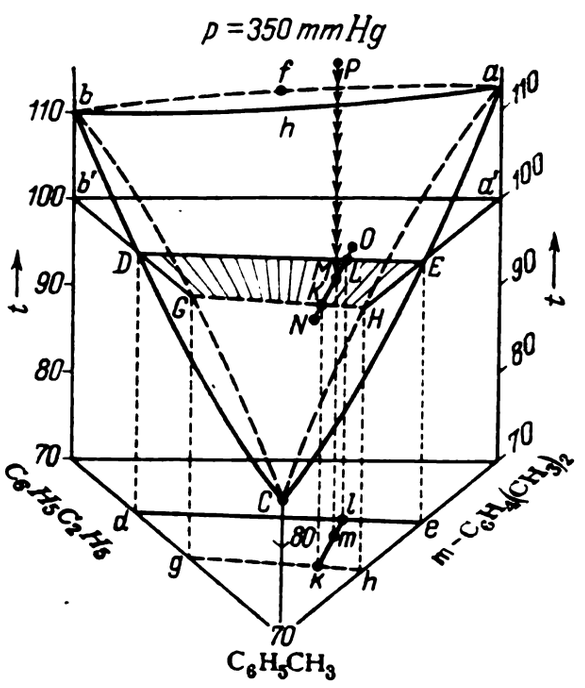


Fig. 142. Temperature-composition diagram.

Liquid-vapour equilibrium isobar in the system m-$C_6H_4(CH_3)_2$-$C_6H_5CH_3$-$C_6H_5C_2H_5$ (see Fig. 141)

11.4.2. Isobar

A liquid-vapour equilibrium diagram for the same system in temperature-composition coordinates at p = const is shown in Fig. 142 (the concentrations in binary mixture AB have been laid off in a direction opposite to that in Fig. 141). Surfaces *CGbfaH* and *CDbhaE* characterize the dry saturated vapour and the boiling liquid, respectively.

Isothermal cross section *b'a'EHGD* gives us tie lines *DG*(*dg*) and *EH*(*eh*) for the isotherm-isobar of the relevant binary mixtures. The figurative points characterizing liquid-vapour equilibrium in

the ternary systems at a given pressure and temperature are in plane *DEHG* between straight lines *DG* and *EH*.

Assume that figurative point $L(l)$ is given on the isotherm of the liquid. Composition $K(k)$ of the saturated vapour will correspond to it (the position of point K is determined by the construction indicated in Fig. 141). In the first approximation, tie lines such as line $KL(kl)$ can be considered straight.

Point M on straight line KL corresponds to a moist vapour containing about 30% of the liquid. Points O and N on its continuation characterize the superheated vapour and the non-boiling liquid, respectively.

Figure 143 shows a developed view of a prism onto whose base the isotherms of the liquid and vapour have been projected (only

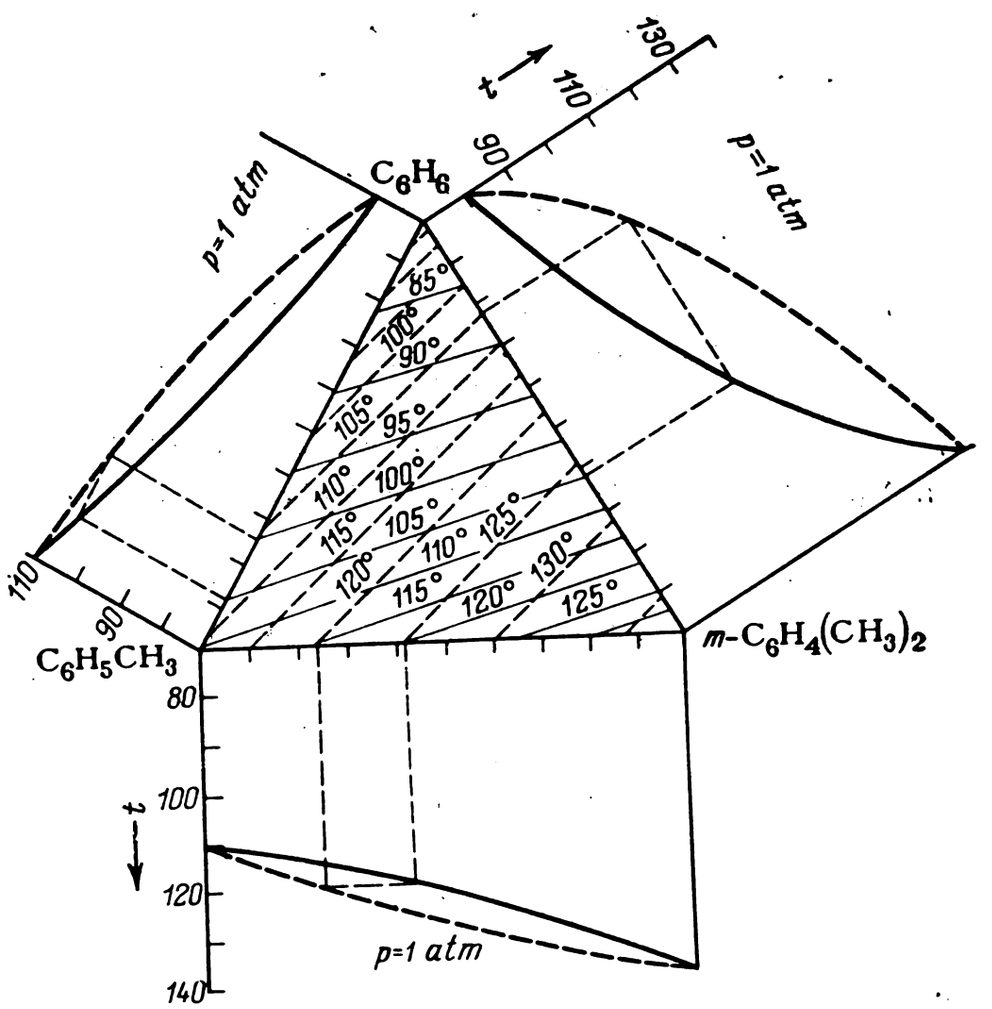


Fig. 143. Developed view of temperature-composition diagram. Equilibrium isobar in the system C_6H_6-$C_6H_5CH_3$-*m*-$C_6H_4(CH_3)_2$

one isotherm is depicted on the sides of the prism). The boiling isotherms are shown by solid lines, the condensation ones by dashed lines.

11.5. DISTRIBUTION OF SOLUTE BETWEEN TWO IMMISCIBLE LIQUIDS

The limiting case of the systems considered in Sec. 11.4 are systems consisting of three substances of which one has been dissolved in two immiscible liquids. The condition of equilibrium in such a system is the equality of the partial molar Gibbs energies of the solute in both phases.

In accordance with the phase rule for a three-component system, the number of degrees of freedom for two phases will be three, therefore $x_2'' = \varphi(p, T, x_2')$. If $p, T = \text{const}$, then $x_2'' = \varphi(x_2')$, and when the concentration of the solute changes by dx_2 new equilibrium will set in. Hence

$$\left(\frac{\partial \overline{G}_2'}{\partial x_2'}\right)_{p,T} dx_2' = \left(\frac{\partial \overline{G}_2''}{\partial x_2''}\right)_{p,T} dx_2''$$

For an ideal solution, in accordance with Eq. (8.44), this equation becomes

$$\left(\frac{x_2'}{x_2''}\right)_{p,T} = \text{const} \quad \text{or} \quad \left(\frac{c_2'}{c_2''}\right)_{p,T} = K \tag{11.3}$$

where c_2' and c_2'' = molar-volume concentrations of the substance distributed between the two phases

K = **partition coefficient.**

Consequently, the relationship between the equilibrium concentrations of the substance distributed between two phases does not depend on its total amount.

Since neither dissociation nor association of the dissolved molecules can occur in ideal solutions, the constant coefficient in Eq. (11.3) does not depend on the concentration for them. Should the solute be in the associated or dissociated state in one of the solvents, however, this problem, which complicates matters, is remedied either by substituting the activities for the concentrations (see Sec. 12.1), or by introducing into Eq. (11.3) a coefficient that is determined on the basis of experimental data from a graph of $\log c_2' = \varphi(\log c_2'')$ (Fig. 144). In the latter case, the equation used for calculations becomes

$$\frac{(c_2')^n}{c_2''} = K \tag{11.4}$$

Equations (11.3) and (11.4) are a quantitative expression of the **Nernst-Shilov distribution law.**

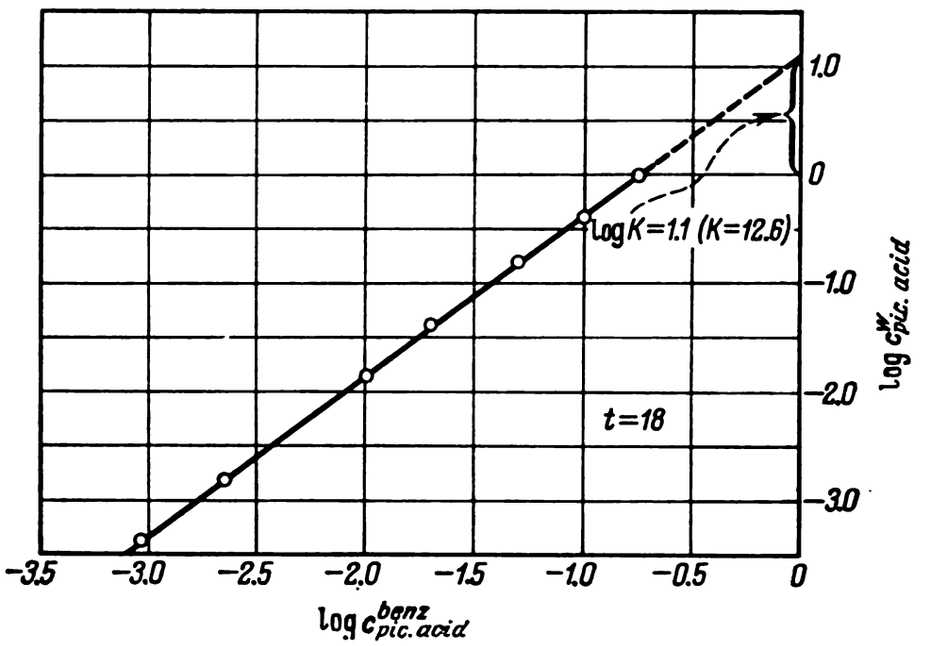


Fig. 144. Distribution of a substance between two immiscible solvents (the concentration is expressed in mol/dm³).
Checking of Eq. (11.4). (See Example 4)

Example 4. The distribution of picric acid between benzene (C_6H_6) and water at 18 °C is characterized by the following data (mol/dm³):

$c^{benz}_{pic.acid}$ ..	0.000 932	0.002 25	0.01	0.02	0.05	0.10	0.18
$c^{w}_{pic.acid}$ ..	0.000 417	0.001 55	0.0142	0.0396	0.156	0.416	0.963

1. Find the equation of the distribution law.

2. What conclusion can be made from the found equation if it is known that picric acid has a normal molecular weight in a benzene solution?

3. Determine the consumption of benzene (in dm³ per dm³ of the aqueous solution) for the extraction of picric acid from an aqueous solution and find the degree of extraction if the aqueous solution contains 50 g of the picric acid per dm³, while the benzene solution should have an acid concentration of 5 g/dm³.

Solution. 1. After plotting a graph in the coordinates $\log c^{w}_{pic.acid} = \varphi(\log c^{benz}_{pic.acid})$ (see Fig. 144) and continuing the straight line up to the axis of ordinates, by Eq. (11.4) we get $\log K = 1.1$ and $K = 12.6$. The slope of the line gives us $n = 1.46$. Hence

$$\frac{c^{w}_{pic.acid}}{(c^{benz}_{pic.acid})^{1.46}} = 12.6$$

or

$$\frac{(c^{benz}_{pic.acid})^{1.46}}{c^{w}_{pic.acid}} = 0.0794$$

2. To solve the second problem, it is more convenient to write down the latter equation in the form

$$\frac{c^{benz}_{pic.\,acid}}{(c^{w}_{pic.\,acid})^{0.686}} = 0.176$$

It thus follows that the picric acid partly dissociates in water.

3. We use the found equation (or Fig. 144) to calculate the equilibrium concentration of the acid in an aqueous solution at $c^{benz}_{pic.acid} = 5/229.1 = 0.0218$ mol/dm³. It equals 0.0474. Therefore, (50/229.1) — 0.0474 = 0.1708 mol of the acid should pass into the benzene solution, for which 0.1708/0.0218 = 7.84 dm³ of benzene are needed. The degree of extraction is 0.1708 × 100/0.2182 = = 78.3%.

Example 5. 1. Find the relationship between the amount x_i of a substance remaining unextracted after each extraction, the initial amount of the substance a to be extracted, the volume of the solution V_0, the volume of each portion of the extractant V_{ex} and the number of extractions n.

2. Use the found relationship to show the effectiveness of extraction by using the total amount of the liquid not at once, but in consecutive portions. Assume for the calculations that $K = 0.2$ (in grammes per gramme), $a = 100$ g, $V_0 = 1$ dm³ and the total volume of the extractant is 1 dm³. Consider two cases: extraction with two and with four equal portions.

Solution. 1. Taking into account the symbols given in the initial conditions, equation (11.3) will become

$$\frac{x_1/V_0}{(a - x_1)/V_{ex}} = K, \quad \frac{x_2/V_0}{(x_1 - x_2)/V_{ex}} = K, \text{ etc.}$$

or

$$x_1 = a\frac{KV_0}{KV_0 + V_{ex}}, \quad x_2 = \frac{x_1 KV_0}{KV_0 + V_{ex}} = a\left(\frac{KV_0}{KV_0 + V_{ex}}\right)^2, \text{ etc.}$$

or after n extractions

$$x_n = a\left(\frac{KV_0}{KV_0 + V_{ex}}\right)^n$$

2. If two equal portions were used for extraction, there would remain in the initial solution

$$x_2 = 100\left(\frac{0.2 \times 1}{0.2 \times 1 + 0.5}\right)^2 = 8.16 \text{ g}$$

and after extraction using four portions

$$x_4 = 100\left(\frac{0.2 \times 1}{0.2 \times 1 + 0.25}\right)^4 = 3.90 \text{ g}$$

which corresponds to degrees of extraction of 91.84 and 96.10%, respectively. If 1 dm^3 of the extractant were used for processing the solution at once, the degree of extraction would be only 83.4%.

Although these calculations are based on the constancy of the coefficient in Eq. (11.3), this assumption is not observed as a rule (see, for instance, the initial conditions of the preceding example). The growth in K with lowering of the concentration, however, makes two or three extractions sufficient in practice.

11.6. FOUR-COMPONENT SYSTEMS

11.6.1. Solution of Three Salts with a Common Ion

The Substances Do Not React. A diagram similar to that depicted in Fig. 127*a* is constructed on each face of a tetrahedron. If we add salt D to eutonic solution E_1 of salts B and C, then the mutual solubility of B and C in water will lower, and its change will be shown by curve E_1E. At quaternary eutonic point E, the solution will be saturated with all the salts. Similar curves E_3E and E_2E characterize the solubility of the corresponding pairs of salts in the presence of the third salt. Therefore, surfaces bE_3EE_1, E_3dE_2E and E_2EE_1c are fields of freezing out of B, D and C.

For practical application, it is more convenient to use not the orthogonal projection employed for ternary systems, but a clinographic (axonometric) one. It is obtained by drawing straight lines through apex A (H_2O) and through the points being projected (Fig. 145). * It is more convenient than an orthogonal projection because the paths of freezing are shown by straight lines. Therefore, for example, the evaporation of the solvent from an unsaturated solution is shown by a fixed point. (In both cases, the composition of only the salt mass is given.)

We shall consider the process of isothermal evaporation of unsaturated solution P (see Fig. 145). Up to saturation of the solution, the projection of point P remains stationary (point P_1). Point l_1 corresponds to the beginning of freezing of B out of the solution, which results in a change in the salt composition of the solution and, accordingly, in shifting of the projection of the point. Since C and D remain in the solution, i.e. the ratio between them does not change,

* These straight lines are drawn only partly in the following figures.

the freezing path in the diagram is on the continuation of straight line $bl_1(BP_1)$. Curve $l_1l_2(P_1P_2)$ corresponds to the freezing out of B. Point l_2 corresponds to the beginning of joint freezing out of B and D. At this moment, the ratio of the amount of frozen-out salt to that

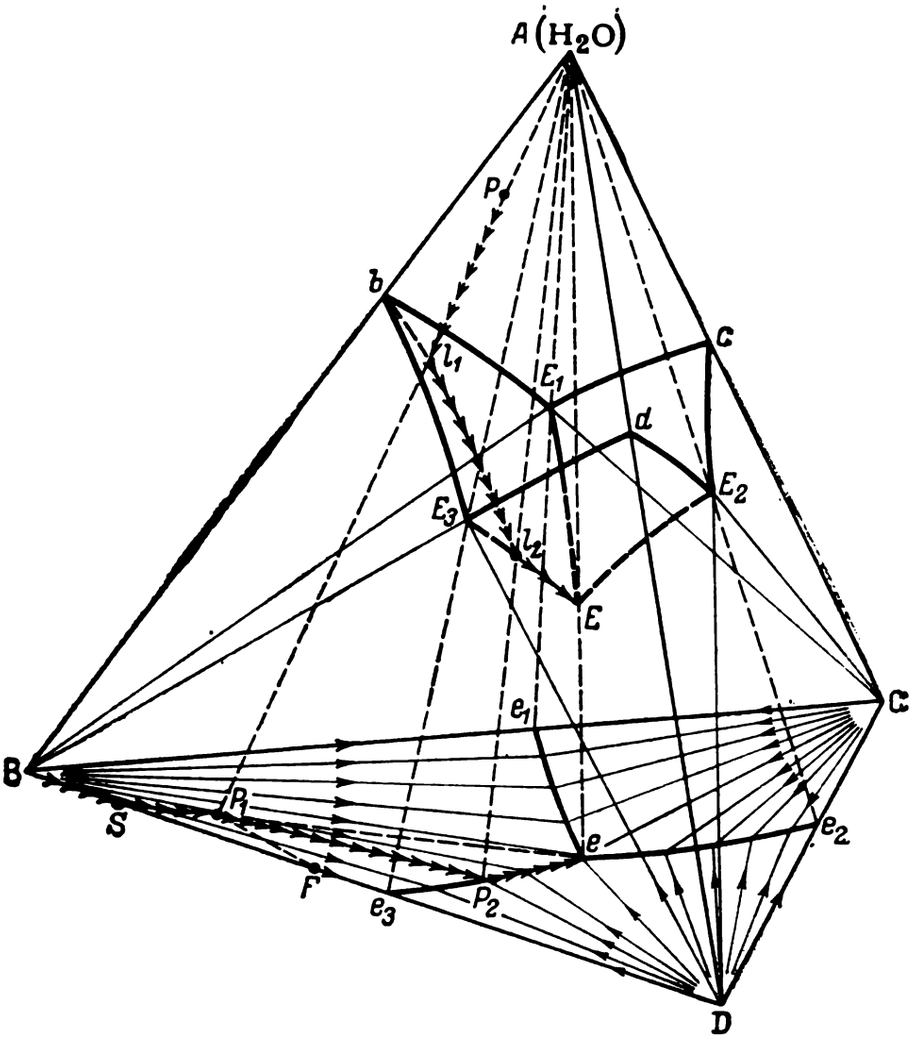


Fig. 145. Isotherm of solubility in water of three common-ion salts that do not react (schematic diagram)

of the remaining salts will be $P_1P_2 : P_1B$, while the yield of B (with respect to the sum of the salts in the solution) will be expressed by line DF, because from the condition of parallelism of straight lines P_1F and P_2D it follows that $P_1P_2 : BP_2 = DF : BD = DF : 100\%$. Both salts will freeze out together up to point E. By this moment, the solid phase becomes enriched with D up to composition S, because in accordance with the tie line rule, the projections of the points characterizing the composition of liquid phase (e), the solid mass (S) and the mixture as a whole (P_1) must be on one straight line. Thus, in the process of freezing out of D, the composition of the solid phase will change along BP. Point $E(e)$ will correspond to freezing out of all three salts, i.e. the figur-

ative point of the solid mixture in the diagram will move from S to P_1. Point P_1 will characterize a completely dehydrated system.

Thus, this diagram is similar to that shown in Fig. 125 (p. 363), and the process of isothermal evaporation in the given system is similar to the cooling process in a three-component system.

One of the Salts Forms a Crystallohydrate. The diagram will acquire the form shown in Fig. 146 (H stands for the crystallohydrate, face ABC coincides with Fig. 129*a*, p. 374). Plane $Be_3d_1''d_1$

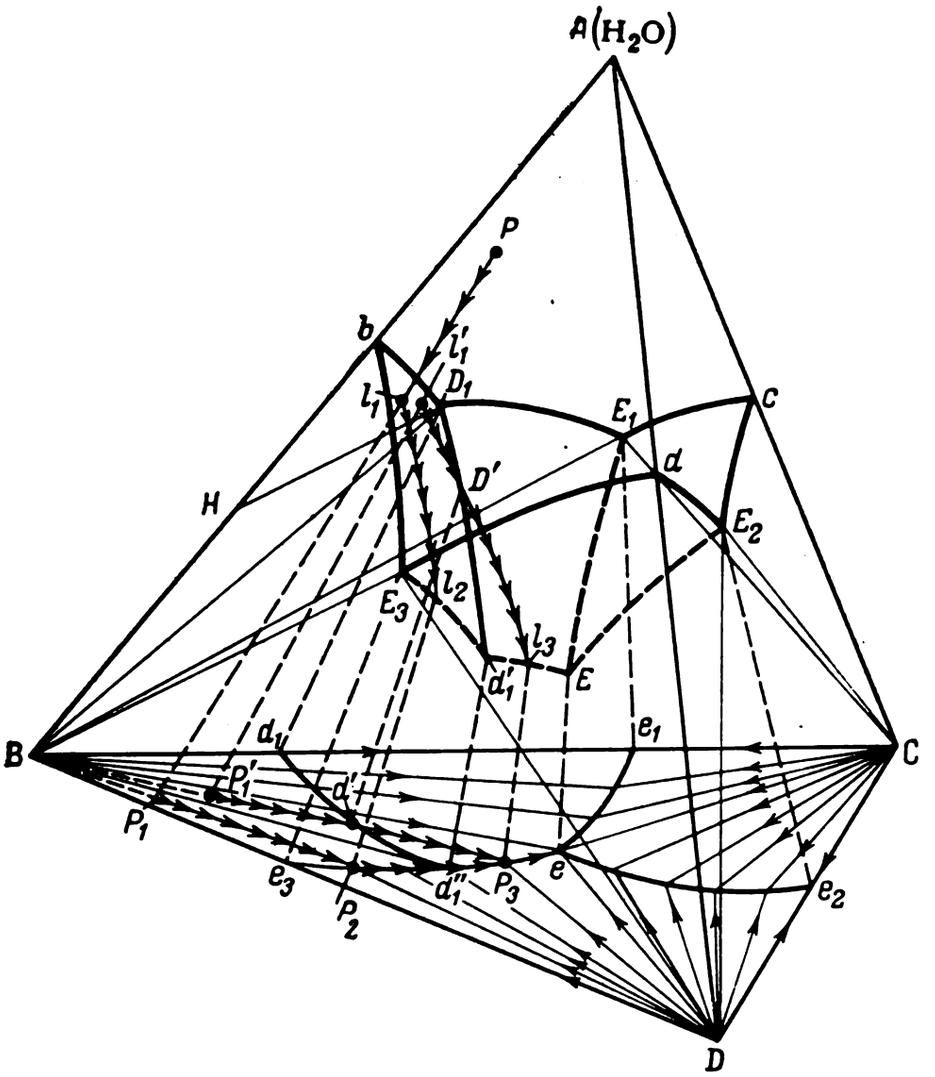


Fig. 146. Isotherm of solubility in water of three common-ion salts, one of which forms a crystallohydrate (schematic diagram)

is a clinographic projection of the freezing field of H, plane $d_1''ee_1d_1$ is the projection of the freezing field of anhydrous salt B, and planes e_1Ce_2e and $e_3d_1''ee_2D$ are the projections of the freezing fields of C and D.

Since the projections of points H and B of the composition coincide, the path of freezing out in the field of B is a continuation of that in the field of H.

Upon the evaporation of solution P, point $l_1(P_1)$ will correspond to the beginning of freezing out of H, and point $l_2(P_2)$ to the beginning of freezing out of D together with H. Both salts freeze out jointly up to point $d_1'(d_1'')$, which corresponds to the beginning of dehydration of the previously frozen-out H. From this moment, the system is invariant ($f = 4 - 1 - 5 + 2 = 0$). After dissolving (dehydration) of all the H, the system will become univariant, and joint freezing out of B and D from the solution will take place. The figurative point will begin to move from $d_1'(d_1'')$ to $E(e)$. Point $E(e)$ will be characterized by the joint freezing of B, D and C. This process terminates not at point d_1'', but at point e, because d_1'', unlike e, is incongruent. Let us use the rule of the triangle (see p. 377) : point d_1'' corresponds to equilibrium of B, H and D ; since the points coincide for the first two salts, the triangle formed by the figurative points of the three solid phases transforms into a straight line (BD). Point d_1'' is outside of this line, therefore it is a transition point and no freezing out of D occurs at it. Conversely, point e corresponds to equilibrium of solid B, C and D, and hence it is a eutonic point.

Consider the case when the figurative point of the initial solution is in the same region, but on the straight line between lines Bd_1'' and BC. The following will occur upon isothermal evaporation : point $l_1'(P_1')$ corresponds to the beginning of freezing of H, point $D'(d')$ to the beginning of dehydration. After all of the previously frozen-out H becomes dehydrated, freezing out of the anhydrous salt will begin (which movement of the point in the previous direction will correspond to). Point $l_3(P_3)$ corresponds to the beginning of freezing out of D together with B (curve P_3e), after which (point e) three salts will freeze out. If the initial point is in sector CBe, then after intersecting curve d_1d_1'' the straight line of evaporation will terminate at the point where it meets curve e_1e (this point corresponds to the beginning of joint freezing out of B and C), and the figurative point will turn toward eutonic point e.

Double Salts. A diagram for congruent solubility has the form schematically shown in Fig. 147 (eutonic points e and e' are congruent), and for incongruent solubility — the form shown in Fig. 148 (eutonic point e' is congruent, transition point d' is incongruent) (cf. Figs. 148 and 131). In these diagrams, plane $aE_1EE_4(Ae_1ee_4)$ and, correspondingly, $adEE_3(Ad_1d'e_3)$ are the freezing fields of A (or if a crystallohydrate is present — the freezing fields of the hydrate) ; plane $E_1E_2E'E(e_1e_2e'e)$ and, correspondingly,

$dE_1E'E(d_1e_1e'd')$ are the freezing fields of a double salt; the remaining two sections of the projection are the freezing fields of the pure substances.

Consider Fig. 147. Here two cases should be distinguished, as for the relevant ternary systems: depending on where the initial

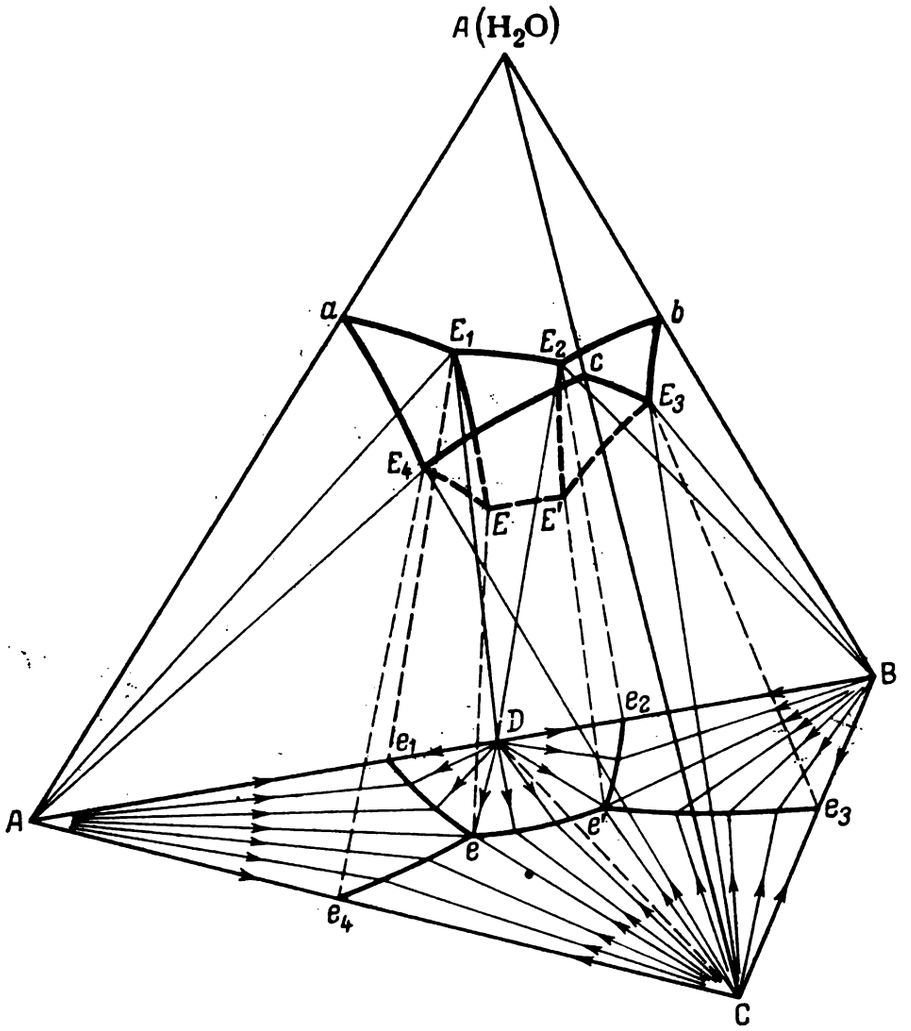


Fig. 147. Isotherm of solubility in water of three common-ion salts forming a congruently soluble double salt (schematic diagram)

point is — to the left or the right of line CD — evaporation will terminate at eutonic e or e'. If the point is on this straight line, the process will terminate at the point of intersection of DC and ee', even though the latter point is not invariant (movement of the straight line of evaporation along line e-e' would indicate a change in the ratio between A and B in the solution, which is impossible).

Now consider Fig. 148. A feature of this system is that point d' is outside of triangle ADC. Five cases are possible here, depending on the location of the initial point.

1. The point is in triangle CFA. Freezing out of A (or C) is followed by joint freezing out of A and C; when point d' is reached,

freezing out of D will begin with the simultaneous dissolving of A. The explanation of the latter fact is that D is relatively richer in A than solution d'. The composition of the liquid phase is constant up to its complete evaporation, and at the end of the process part of the previously frozen-out A will remain.

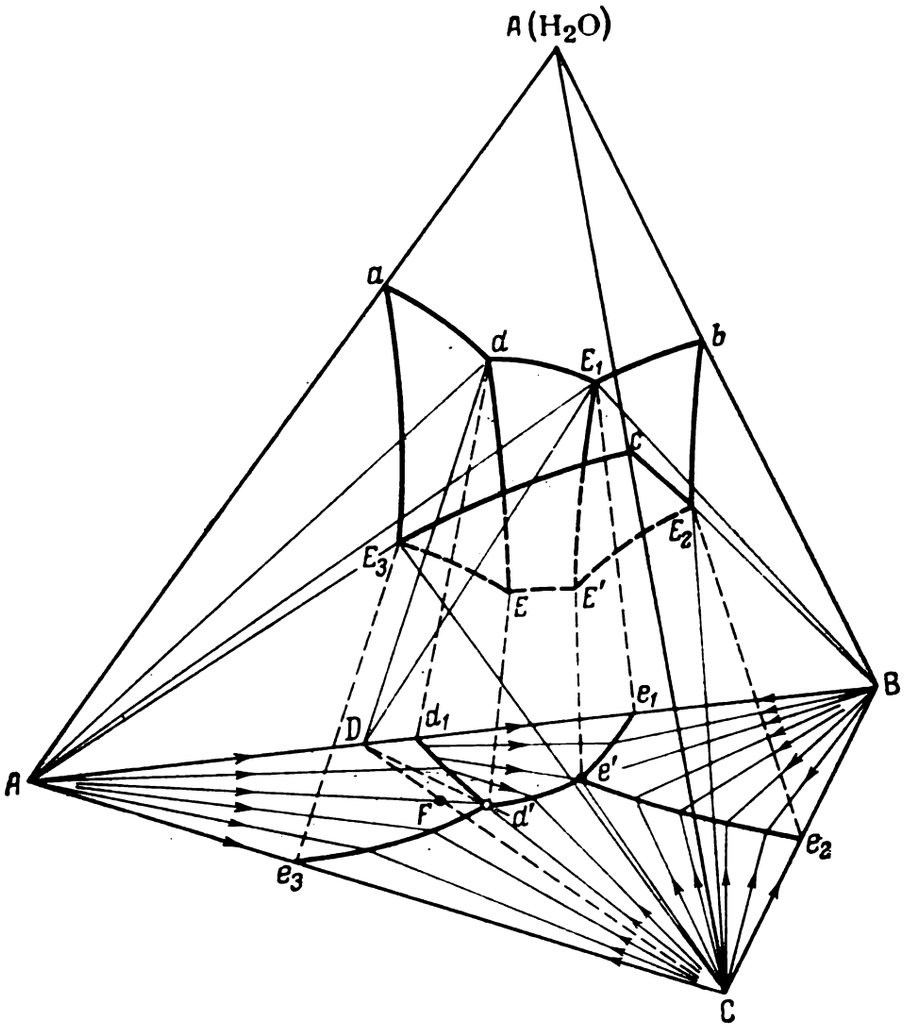


Fig. 148. Isotherm of solubility in water of three common-ion salts forming an incongruently soluble double salt (schematic diagram)

2. The point is in triangle $Cd'F$. This differs from the preceding case in the following: since the solution is poorer in A than in D, the process indicated in the first case will end before dehydration of the solution. Therefore, after complete transformation of the frozen-out salt A into D, the freezing out of D and C continues, which corresponds to movement of point d' to e'. When composition e' is reached, these salts will freeze out jointly with B, after which the solution becomes dehydrated without a change in its composition.

3. The point is in triangle AFD. After freezing (process d_1d'), A again dissolves and D freezes out. At composition d' and the con-

tinuing dissolving of A, salt C begins to freeze out together with D. At a content of the salts corresponding to point d', the solution becomes completely dehydrated (before all of A dissolves).

4. The point is in triangle $Dd'F$. This differs from the preceding case in that at composition d' the solution will not become dehydrated up to the complete dissolving of A; therefore freezing will continue along curve $d'e'$ and will terminate at e' (see case 2).

5. The point is in triangle d_1Dd'. First the process coincides with those considered in cases 3 and 4. When the position of the point on curve d_1d' coincides with the point of intersection of the cooling straight line drawn through the initial point to point D, the process will correspond to movement of the figurative point along the continuation of this line. This means that dissolving of A will terminate, and only freezing of D will continue. Next (the process gets onto curve $d'e'$) joint freezing of D and C will begin, after which (point e') D, C and B freeze out.

Water Diagram. A polythermal diagram can be used for calculations involving a change in temperature. It is more convenient, however, to use **water diagrams.**

Let us erect perpendiculars to the plane of the projection of an isothermal diagram and lay off on them the content of water in the solution (in moles per 1 or 100 equivalents of the sum of the salts in the solution whose salt composition is depicted by the point at the base of a perpendicular). If we connect the ends of the perpendiculars corresponding to the composition of saturated solutions, we shall get a diagram (Fig. 149) whose surface consists of the freezing fields of the corresponding substances. A water diagram is thus a modification of the diagram shown in Fig. 145. The processes of isothermal evaporation (or dilution) in both diagrams are identical. The only difference is that in the former they are depicted by slanting lines, and in the latter by vertical lines. Since in a water diagram the points corresponding to pure water are at infinity, the lever rule cannot be applied here in a vertical direction.

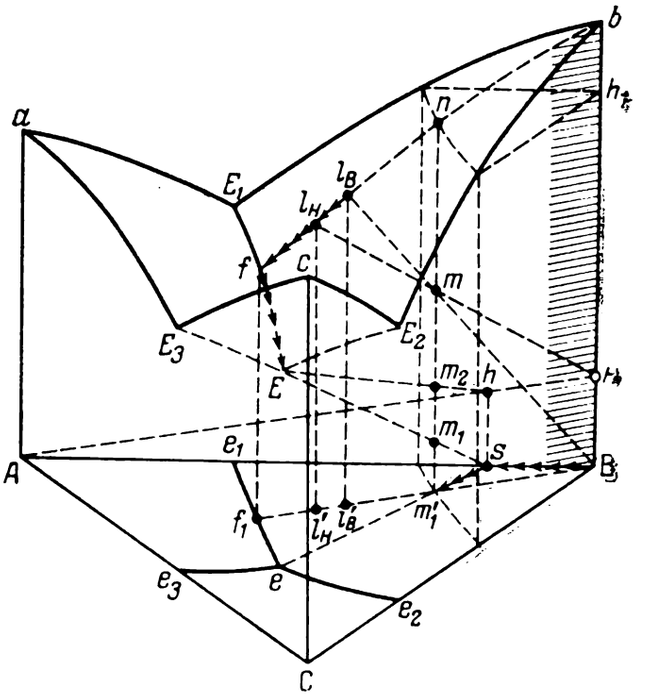


Fig. 149. Water diagram for solutions of three common-ion salts (schematic diagram)

In addition, a water diagram is characterized by the following feature: if points A, B and C and points on the corresponding sides of the base correspond to solid phases for simple and double salts, then the points of the crystallohydrates of simple and double salts are higher than these points (at a height corresponding to the content of water in the crystallohydrate).

Attention should be given to a certain external similarity between the diagram being considered and that in Fig. 125 (p. 363): the projection onto the base of planes of equal water content (called **isohydric**) is similar to the isothermal projections in Fig. 125 (one such cross section — isohydric section h_1 — is shown in Fig. 149).

When an unsaturated solution is cooled, the composition of the system does not change, and therefore the point of the system remains stationary. Lowering the solubility is attended by an increase in the water content in a saturated solution, and movement of the freezing field to the point of the system will correspond to this. The solid phase will begin to form as soon as the solution becomes supersaturated. At this moment, the point of the system in the water diagram will be under the freezing surface (the number and nature of the freezing-out salts will depend on the "freezing volume" which the initial point is in).

Assume that the system has composition m. Let us draw surface $fbBf_1$ perpendicular to the base of the prism through this point and the edge of the prism corresponding to the freezing-out salt (for purposes of illustration part of this surface is shaded in the figure). If B freezes out from mixture m, then according to the straight tie line rule, the state of the saturated solution will be depicted by point $l_B(l'_B)$. If H freezes out from the solution, its composition will be depicted by point $l_H(l'_H)$. Both these points characterizing the composition of the liquid phase after cooling will naturally lie on the straight line of freezing of B and H, i.e. on the continuation of line bn.

The decrease in the water content in the initial solution, which lowering of point m corresponds to, will cause points l_B and l_H to lower also. When the water content diminishes to such an extent that these points will be below f, A will begin to freeze out together with B (or H), and the composition of the saturated solution will be depicted by a point on "watershed" E_1E below point f. Therefore, the point of the solid mixture will begin to move from B to A or, when the crystallohydrate freezes out, from H to A. When the composition of the saturated solution is characterized by point $E(e)$, the solid mixture will have composition s (h if the crystallohydrate freezes out). Consequently, for all three salts to freeze out instead of two, the initial composition of the system must correspond to point m_1 for freezing out of an anhydrous salt, and to point m_2

for freezing out of a crystallohydrate (the lines with arrows show the process of the change in composition of the liquid and solid phases for the freezing out of an anhydrous salt).

11.6.2. Solution of Salts with Different Ions (Mutual Pairs)

An isotherm of the solubility in water of four salts forming mutual pairs (see Sec. 11.1.2) is shown in Fig. 150. Surfaces $aE_2E'E_1$, $E_2bE_3E''E'$, E_3cE_4E'' and $dE_4E''E'E_1$ are freezing fields of salts CM,

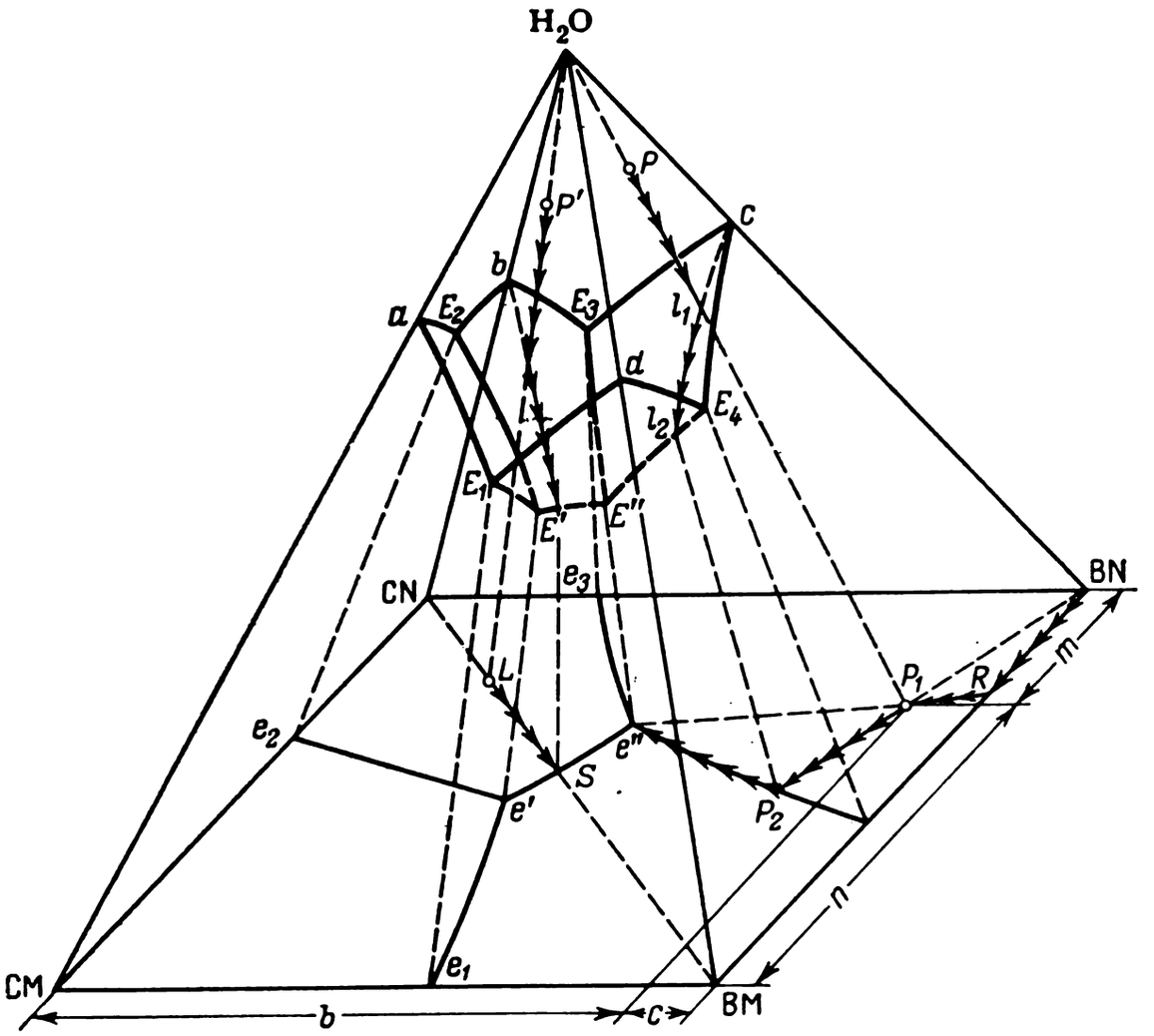


Fig. 150. Isotherm of solubility in water of four salts forming mutual pairs (schematic diagram)

CN, BN and BM, respectively. Lines E_2E', E_3E'', E_4E'' and E_1E' are lines of joint freezing of the corresponding salts; E_1, E_2, E_3 and E_4 are double eutonics, and E' and E'' are triple eutonics. The lower-case letters also indicate the points in the clinographic projection (the water content is not shown in the horizontal projection).

Lines *CN-BN* and *CM-BM* characterize solutions containing 100% of anion N and 100% of anion M, respectively. Lines *CM-CN* and *BM-BN* correspond to 100% of cation C and 100% of cation B. Consequently, if the composition of the salt mass $m\mathrm{M} + n\mathrm{N} + b\mathrm{B} + c\mathrm{C}$ is given, it will be depicted by point $P(P_1)$. When a system includes ions of different valencies, the corresponding multiple quantities are used for the ion with the lower valency (for example Na_2Cl_2 in conjunction with bivalent ions, Na_3Cl_3 with trivalent ions, etc.).

To assess the amount of water in a system, a water diagram is constructed, the water content being laid off along a vertical line, i.e. a pyramid is replaced with a prism. Drawing isohydric planes at different heights and projecting their cross sections by the freezing field onto the base of the prism, we get the graph shown in Fig. 151.

The process of isothermal evaporation of solution P' after considering a similar process for a solution of three salts with a common ion (see Figs. 145 and 146) requires no additional discussion (up to the moment of freezing of the three salts). Attention should only be given to the following.

1. If the triple eutonic is in the "composition triangle" whose apices are the salts entering the solution, the freezing process will terminate at this eutonic, i.e. the solution at this point will be congruently saturated (point e'' in Fig. 150 for solution P_1). Indeed, in accordance with the phase rule $f = 4 - 5 + 2 = 1$ at $t = \text{const}$, we get $f_{\text{cond}} = 0$, i.e. everything is fixed (including the concentration of the solution).

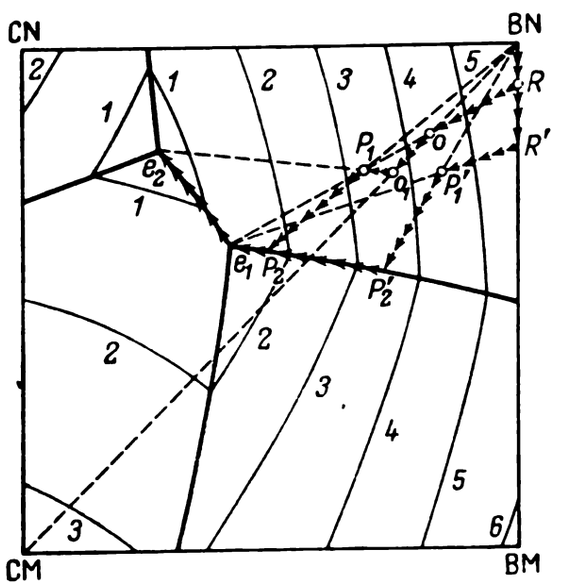


Fig. 151. Projection of isotherm of solubility in water of four salts forming mutual pairs (schematic diagram)

2. If the triple eutonic is outside of the composition triangle whose apices are the salts entering the solution, the constancy of the composition of the liquid phase in the process of freezing (the system is invariant at $t = \text{const}$) will be due to the dissolving of one of the salts (BM in the given case), i.e. to the process BM (from the frozen-out solid) + CN (from the solution) = BN(c) + CM(c). Conse-

quently, eutonic point e_1 (see Fig. 151) will be incongruent. Here three cases are possible:

(a) the initial point is farther from apex BM than diagonal CM-BN (point P_1, Fig. 151). The salt composition of the solution changes along line P_1-P_2-e_1 as the water evaporates. When point e_1 is reached, the solid will have composition R. After this, the process indicated above begins, which will result in the appearance of salt CM in the solid phase; therefore point R will move in the direction of e_1. When point o is reached, the previously frozen-out BM will be completely used up, and since CM and BN continue to freeze out from the remaining solution, the composition of the liquid will begin to change along curve e_1-e_2, and that of the solid along line o-o_1 (because it will contain only two salts — CM and BN). When congruent eutonic e_2 is reached, freezing out of three salts (CN, BN and CM) will begin, the system will again become invariant, and when with respect to the composition of the salt mixture point o_1 reaches initial point P_1, the entire mixture will be dried up;

(b) the initial point is closer to apex BM than diagonal CM-BN (point P_1'). The composition of the solution during evaporation will change along curve P_1'-P_2'-e_1, and the composition of the salt mixture along line [BN]-R'-P_1'. Since points P_1' and e_1 are at different sides of diagonal CM-BN, so much of salt BM will freeze out before it begins to dissolve that the solution will vanish before this salt does, i.e. the process will terminate at point e_1;

(c) the initial point is on diagonal CM-BN (for example at point o_1); the process will terminate at point e_1 with the simultaneous vanishing of BM and CN, i.e. the salt mass will be a mixture of CM and BN.

3. The line of triple eutonics intersects the diagonal of the square and thus both eutonics are congruent. When any solution with a figurative point on this diagonal, for example $P'(L)$ in Fig. 150, is cooled, freezing out of the component in whose field the initial point is will be followed by freezing out of the "adjacent" salt. Since both salts freeze out in the same ratio in which they are in the solution, the process terminates at this point (point S). Thus, at S the solution is completely dehydrated, although the system is not invariant ($f = 4 - 4 + 2 = 2$ and at $t = \text{const}$ we have $f_{cond} = 1$).

4. A change in temperature is attended by a change in the concentration of a saturated solution, therefore both the position of

the curves on the horizontal projection (Fig. 152) and the size of the freezing fields will change. In this connection, the saturated solution may be in a field saturated with a different salt, and the

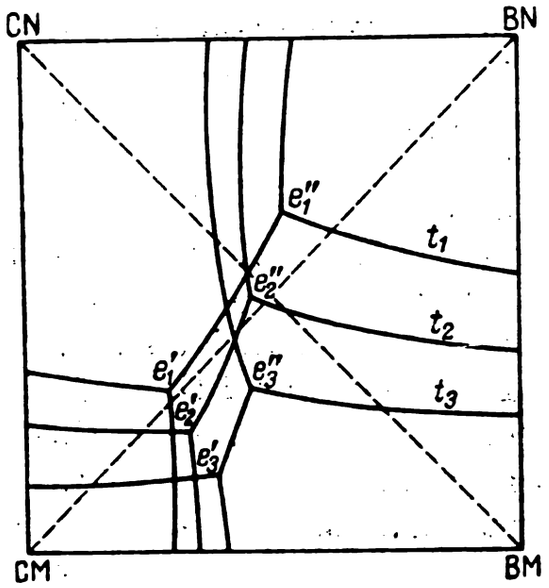


Fig. 152. Projection of isotherms of solubility in water of four salts forming mutual pairs (schematic diagram)

triple eutonic may transform from a congruent to an incongruent one and vice versa. All this permits us to indicate a specific way of changing the temperature to freeze out the corresponding salt.

Chapter 12

ACTIVITIES

12.1. BASIC CONCEPTS AND DEFINITIONS

In non-ideal solutions, the concentration stops being a quantity unambiguously characterizing a solution. The various corrections introduced to take a quantitative account of the factors distinguishing a real solution from an ideal one by no means always give satisfactory results, and if they do, this is only at the cost of considerable complications. This creates much practical inconvenience.

It has been indicated in a previous chapter that for real systems the fugacity should be substituted for the pressure, and the activity for the concentration. The activity, and not the stoichiometric concentration, is a measure of the real action of a substance in solutions when any equilibrium sets in, including chemical and electrochemical processes, and the distribution between phases. It is very important that the activity may be substituted for the concentration, just as the fugacity for the pressure, only in equations characterizing equilibrium. With such a substitution, for example, the distribution law for any systems becomes

$$\frac{a_2'}{a_2''} = \text{const}$$

because the need to have exponents which take account of the non-ideal nature of solutions [Eq. (11.4)] vanishes.

Like fugacity, activity can be called the effective concentration at which an ideal solution acquires the thermodynamic properties of the given real solution. By introducing the activity, we purely *formally* take into account the reaction between the molecules of the solvent, the effect of hydration, the electrostatic attraction between ions (for a solution of electrolytes), in short everything that distinguishes a real solution from an ideal one and that, strictly speaking, does not lend itself at present to quantitative calculation.

The need to substitute the activity for the concentration naturally appears for electrolytes at lower concentrations than for non-elec-

trolytes. It is also general knowledge that no expressions which according to the theory of electrolytic dissociation include the concentration are true for strong electrolytes (anomalies in the osmotic pressure, electric conductivity, e.m.f.). When activities are substituted for concentrations, these anomalies may be disregarded.

The ratio between the activity of a component of a solution and its concentration is called the **activity coefficient**. In accordance with the different expressions for the concentration of a solution, the activity coefficients are written down as follows:

$$\gamma_i = \frac{a_i}{m_i}; \quad y_i = \frac{a_i}{c_i} \quad \text{and} \quad f_i = \frac{a_i}{x_i} \tag{12.1}$$

The relationship between these coefficients can be found from that between m_i, c_i and x_i. For dilute solutions, these coefficients are equal or almost equal to one another. Thus, for a monovalent electrolyte, the difference between y_i and f_i up to $c_i = 0.1M$ does not exceed 0.3%, and up to $c_i = 1M$ is 1.7%. For this reason, we shall use only γ_i in the following, although, strictly speaking, Eq. (12.25) should contain y_i, and Eqs. (12.27)-(12-32) f_i.

The activity of an electrolyte is determined by the product of the activity of its ions. Since at infinite dilution, the activity of each of the ions becomes identical to its stoichiometric concentration, then assuming complete dissociation and thus explaining the anomalies of solutions only by the forces acting in them, we may extend this rule to any solution.

It is convenient to take the state in which (for a binary electrolyte) $a_+a_- = 1$ as the standard one. Hence for an electrolyte whose molecule decomposes into ν ions (ν_+ positive and ν_- negative ones), the activity will be determined by the equation

$$a = a_+^{\nu_+} a_-^{\nu_-} \tag{12.2}$$

Since ions of one sign cannot be obtained in an isolated form, while in concentrated solutions $a_+ \neq a_-$, it is impossible to determine directly the activities of separate ions. It is therefore expedient to introduce the concept of the geometric mean activity of ions

$$a_\pm = (a_+^{\nu_+} a_-^{\nu_-})^{\frac{1}{\nu}} = \sqrt[\nu]{\alpha} \tag{12.3}$$

where $\nu = \nu_+ + \nu_-$.

The activity coefficient of an electrolyte is determined by the quantity

$$\gamma_\pm = \frac{a_\pm}{m_\pm} \tag{12.4}$$

which in the limiting case for an infinitely dilute solution coincides with the apparent degree of dissociation α (Fig. 153).

Combining Eqs. (12.3) and (12.4), we get

$$a = (m_{\pm}\gamma_{\pm})^{\nu} \quad (12.5)$$

In the same way as $(f/p)_{p\to 0}\to 1$, the ratio of activity to concentration when the latter diminishes tends to unity; for an infinitely dilute solution the activities coincide with the concentrations.

In accordance with the definition of activity

$$\mu_i = RT \ln a_i + \mu_i^{\circ}(p, T)$$

or

$$\bar{G}_i = RT \ln a_i + \text{const} = RT \ln \gamma_i + RT \ln m_i + \text{const} \quad (12.6)$$

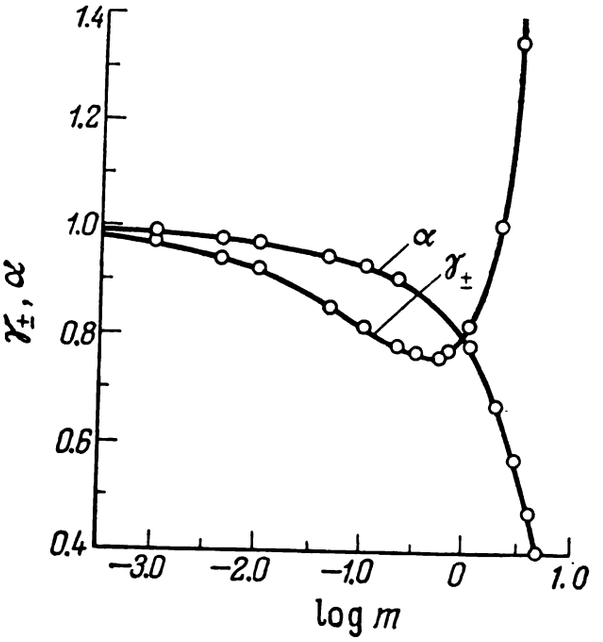


Fig. 153. Dependence of the apparent degree of dissociation and the activity coefficient of HCl at $t = 25$ °C on the concentration of the hydrochloric acid

The activity coefficient, whose expression for an ideal solution was already given in Sec. 8.4, in accordance with Eq. (12.6) corresponds to the additional work which ought to be done at p, $T = \text{const}$ to overcome the force of interaction when one mole of a component of an ideal solution is transferred into a real solution having the same concentration. This work diminishes with increasing dilution, and for an ideal solution, according to Eq. (8.43), it becomes equal to zero. Conversely, in concentrated solutions, the work done in dilution to overcome the attraction between separate particles, especially if the latter carry a charge, becomes so significant that the activity coefficient exceeds unity (see Fig. 153), and the activity (effective concentration) becomes greater than the actual concentration.

The minimum of the isotherm $\gamma_{\pm} = \varphi(m)$ (see Fig. 153) is typical (for some substances it is in the region of very great concentrations). It can therefore be considered that for electrolytes-analogues the values of $(\gamma_{\pm})_{\min}$ form a regular system. This is confirmed for one example in Fig. 154. Although the amount of available data is very scant, a glance at the figure clearly shows both the periodic nature of $(\gamma_{\pm})_{\min}$ and the circumstance that the points in accordance with the charge of the cation mainly group around three descending curves, the growth in the atomic number Z appreciably affecting the rate of falling of $(\gamma_{\pm})_{\min}$ for MeCl, having a smaller influence for $MeCl_2$ and almost no influence for $MeCl_3$.

According to Eq. (12.6), the activity is a relative quantity. Its value can be computed with an accuracy up to a constant independent of the concentration, this constant being equal to the partial

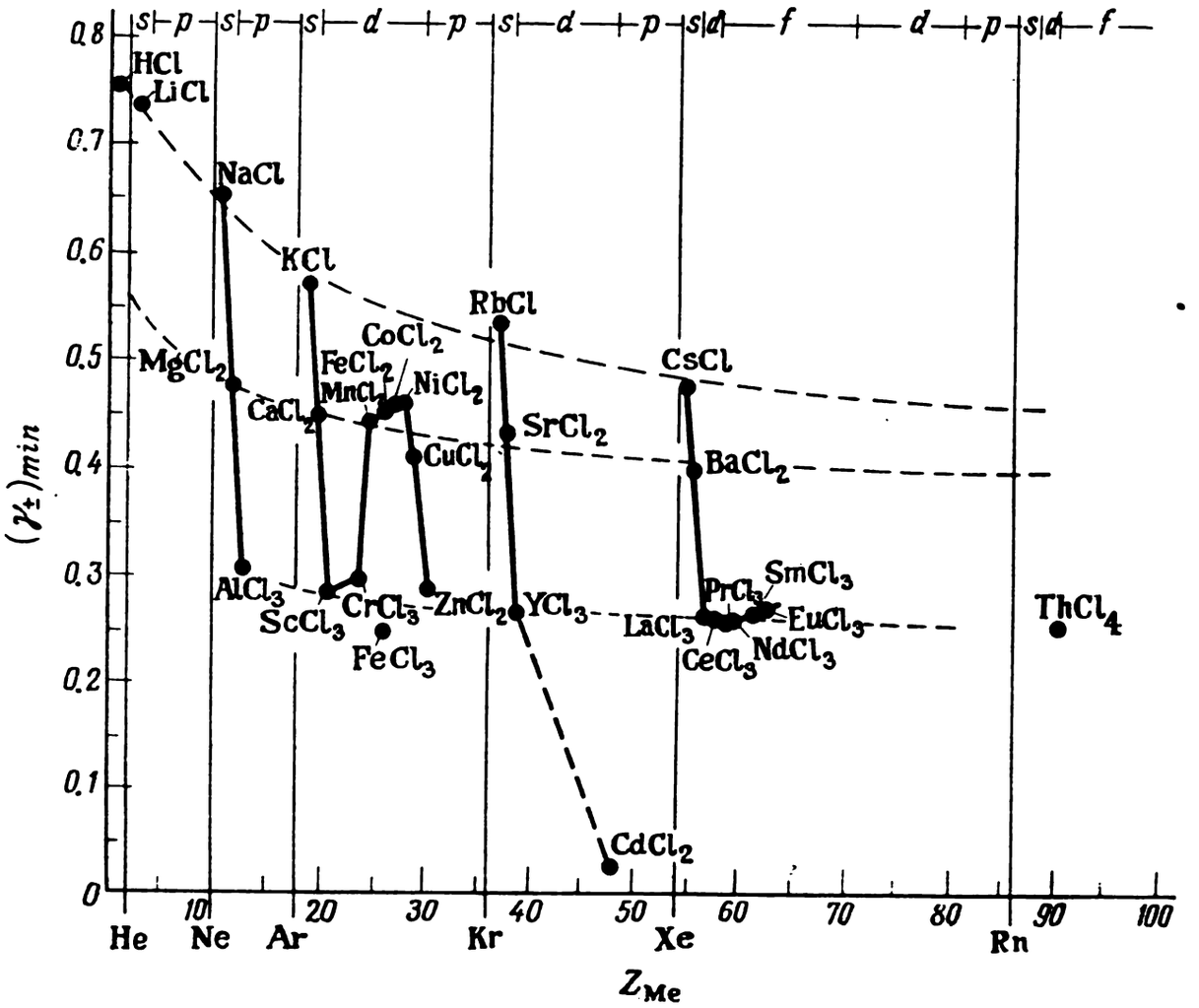


Fig. 154. Relationship between the activity coefficient of aqueous solutions of $MeCl_n$ at 25 °C at the point of a minimum on the curves $\gamma_\pm = \varphi(m)$ and the atomic number Z_{Me} of a metal

molar Gibbs energy of the relevant component of the solution in the standard state.

Consequently, the difference between the partial molar Gibbs energy in the state which the activity a_i corresponds to and the Gibbs energy in the standard state, when $a_i = 1$, is expressed by the equation

$$\bar{G}_i - G_i^\circ = RT \ln a_i \qquad (12.7)$$

If we must resort to calculating the fugacities in order to determine the properties of real gases, then for non-ideal solutions we must compute the activities. Establishment of the relationship between the activity on one hand and the temperature, pressure

and concentration on the other permits us to apply thermodynamic laws to real solutions.

The activity of a given component in each case should be related to the same standard state, chosen by considerations of convenience.

The state of the pure solvent is generally adopted as the standard state for a solvent, i.e. it is assumed that

$$a_1^\circ = x_1^\circ = 1$$

For a solute (for which the concept of activity is especially important), it is good to select a state in an infinitely dilute solution as the standard one, when the activity of the substance becomes equal to the concentration:

$$a_2^\circ = a_2^* = m_2^*$$

(here, as throughout the following, the superscript * relates to an infinitely low concentration, i.e. to infinite dilution). Thus, the standard state of a solvent and solute will be their state in an infinitely dilute solution in which the activities equal the concentrations.

If the activity of one of the components of a solution is known, or more precisely the dependence of the activity on the concentration, then the activity of the second component (in the case of a binary solution) is determined by Eq. (8.47), which in accordance with Eq. (12.7) becomes

$$x_1 \, d \ln a_1 + x_2 \, d \ln a_2 = 0$$

or

$$d \ln a_2 = -\frac{x_1}{x_2} d \ln a_1 = -\frac{55.51}{m} d \ln a_1 \qquad (12.8)$$

or in accordance with Eq. (12.1)

$$x_1 \, d \ln \gamma_1 + x_2 \, d \ln \gamma_2 = 0 \qquad (12.9)$$

The pressure dependence of the activity of a solution component is expressed by the equation

$$\left(\frac{\partial \ln a_i}{\partial p}\right)_{T, x} = \frac{\overline{V}_i}{RT} \qquad (12.10)$$

which coincides with Eq. (8.7).

The temperature dependence of the activity is determined by the equation

$$\left(\frac{\partial \ln a_i}{\partial T}\right)_{p, x} = \frac{H_i^\circ - \overline{H}_i}{RT^2} \qquad (12.11)$$

which coincides with Eq. (8.8).

12.2. METHODS OF CALCULATING ACTIVITIES

The methods of calculating the activity are based on the extrapolation of equations holding for all solutions to infinite dilution, when the activities in these equations can be replaced with quantities lending themselves to direct measurement (concentration, saturated vapour pressure, etc.).

Such extrapolation permits us to find appropriate coefficients that will make it possible to calculate the activities on the basis of experimental data upon the reverse transition to finite concentrations.

In addition to this procedure, not involving any assumptions, the activity (activity coefficient) can be calculated using the quantity $\Delta G = RT \ln \gamma$, which corresponds to the work of transfer of one mole of a solute from an ideal to a non-ideal solution at a constant concentration. The theoretical calculation of ΔG requires us to introduce an assumption on the nature and action of the forces causing deviation of a solution from the ideal state. Such calculations have been successful only for quite dilute solutions of electrolytes (they will be briefly described below).

12.2.1. Non-Electrolytes

Calculations According to the Distribution Law. For the equilibrium distribution of a substance between two immiscible solvents with which the substance forms a real solution, Eq. (11.3) becomes $a_2' = Ka_2''$. If the dependence of a_2 on x_2 for one of the solutions is known, the same dependence can be determined for the conjugate solution.

The partition coefficient K is determined from the limiting conditions; since for infinite dilution we have $a_2^* = x_2^*$, then

$$K = \frac{(a_2')^*}{(a_2'')^*} = \frac{(x_2')^*}{(x_2'')^*}$$

Example 1. The distribution of $HgCl_2$ (m.c.) between water (w) and benzene (benz) at 25 °C is characterized by the following data:

$c_{m.c.}^{benz}$	0.000 155	0.000 310	0.000 618	0.005 24	0.012 22	0.021 0
$m_{m.c.}^{w}$	0.001 845	0.003 69	0.007 38	0.064 8	0.157 8	0.286 6

Find the activity of the salt in an aqueous solution in which $m = 0.2866$ and compare it with the concentration of the solution.

Solution. Considering for dilute solutions that $a^{w}_{m.c.} = m$, we find the partition coefficient by dividing m by c:

$$\frac{m}{c} = \frac{0.001\,845}{0.000\,155} = 11.90$$

Since the partition coefficient characterizes equilibrium, we substitute the ratio $a^{w}_{m.c.}/a^{benz}_{m.c.}$ for the ratio m/c at high concentrations. Considering that $a^{w}_{m.c.} = Ka^{benz}_{m.c.}$ (where $K = 11.90$), we get $a^{w}_{m=0.2866} = 11.90 \times 0.0210 = 0.250$, which differs from the value of the concentration by 12.8%.

Calculations According to the Vapour Pressure. If one of the phases is a gas, i.e. equilibrium in the system liquid-vapour is being studied, the equation $a'_2 = Ka''_2$ acquires the form $a_2 = Ka^{g}_2$ (where a_2 is the activity of the solute in the solution).

In a dilute solution, $a^{*}_2 = (x^{lq}_2)^{*}$ and $a^{g}_2 = p_2$; therefore the relationship $a'_2 = Ka''_2$ in accordance with Eq. (8.51) becomes $x^{lq}_2 = K'p_2$, where the value of the coefficient has been extrapolated to infinite dilution. After constructing a graph in the coordinates $x^{lq}_2/p_2 = \varphi(x^{lq}_2)$ according to experimental data and continuing the straight line to $x^{lq}_2 = 0$ (Fig. 155), we find the value of K at the point of its intersection with the axis of ordinates, because at infinite dilution the activity equals the concentration and $K = K'$. Next, by multiplying K in accordance with the equation $a^{lq}_2 = Ka^{g}_2$ by the partial vapour pressure of the solute for various concentrations of it in the solution, we find that $a^{g}_2 = \varphi(x^{lq}_2)$.

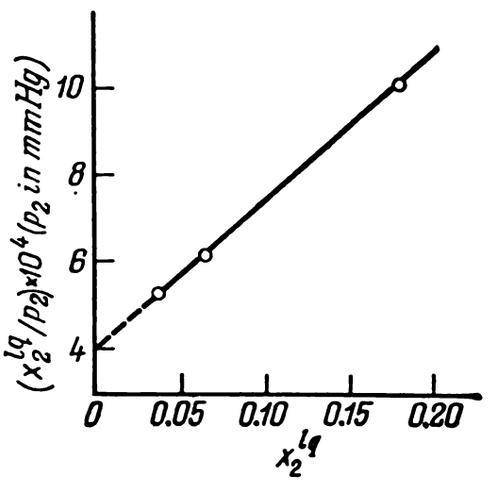


Fig. 155. Determining the activity according to the dependence of the vapour pressure on the composition of a solution (the subscript "2" relates to CH_3COCH_3).

(See Example 2)

We determine the activity of the solvent, following the assumption that its behaviour in the gaseous phase obeys Eq. (8.45), from the ratio of the partial pressure to the saturated vapour pressure of the pure solvent, i.e. with the aid of the equation $a_1 = p_1/p^{\circ}_1$. This method of determining a_1 is especially convenient when the solvent has a measurable vapour pressure.

Example 2. Use the data given in the following table to calculate the activities of the components of a solution of acetone (CH_3COCH_3) in carbon disulphide (CS_2) at different concentrations.

Solution. Taking acetone as the solute and considering its vapour to be an ideal gas, we substitute x_2 for a_2. After calculating the

ratio $x_2^{liq}/p_2 = K'$ for various values of x_2^{liq}, we construct a graph in the coordinates $K' = \varphi(x_2^{liq})$ (see Fig. 155). By extrapolating K' to infinite dilution, we find $(K')^* = K = 0.0004$. Next from

$x_{CS_2} \times 100$	p_{CS_2}, mm Hg	$p_{acetone}$, mm Hg	$x_{CS_2} \times 100$	p_{CS_2}, mm Hg	$p_{acetone}$, mm Hg
0	0	343.8	49.74	404.1	242.1
6.24	110.7	331.0	61.24	426.3	227.0
7.11	123.1	328.7	67.13	438.0	217.0
12.12	191.7	313.5	71.97	447.5	207.1
19.91	271.9	290.6	82.80	464.9	180.2
27.61	323.3	275.2	93.50	491.9	109.4
35.02	358.3	263.9	96.20	500.8	73.4
44.74	390.4	250.2	100	512.3	0

the equation $a_2^{liq}/a_2^g = a_2^{liq}/p_2 = K = 0.0004$, we calculate the activity of acetone at different concentrations.

We take the activity of carbon disulphide equal to the ratio of its partial pressure (at the given concentration) to the vapour pressure of the pure solvent.

The results of the calculations are given below:

$x_1 = x_{c.d}$	0.06	0.07	0.12	0.20	0.275	0.35	0.445
$a_2 = a_{acet}$	0.132	0.132	0.125	0.116	0.110	0.106	0.097
$a_1 = a_{c.d}$	0.216	0.240	0.374	0.531	0.631	0.699	0.762
$x_1 = x_{c.d}$	0.50	0.61	0.67	0.72	0.83	0.935	0.96
$a_2 = a_{acet}$	0.091	0.087	0.083	0.072	0.044	0.029	—
$a_1 = a_{c.d}$	0.789	0.849	0.855	0.874	0.908	0.960	0.97

These results show that the volatility of carbon disulphide at all concentrations is greater than that of acetone. For both components, it is greater than it would be if they retained in the given solution the properties which they would have had in an ideal or infinitely dilute solution (this can also be seen from Fig. 79, p. 283).

Determination of a_1 According to a_2 and a_2 According to a_1. Integration of Eq. (12.9) within the limits from $x_2 = 0$ to a certain concentration x_2 yields

$$\log \frac{a_1}{x_1} = -\int_0^{x_2} \frac{x_2}{x_1} d \log \frac{a_2}{x_2} \qquad (12.12)$$

because $(a_1/x_1)_{x_1=0} = 1$. This equation is solved by graphical integration according to the relationship $a_2 = \varphi(x_2)$ (Fig. 156).

The equation for computing a_2 according to a_1 coincides with Eq. (12.12) except for the subscripts, but the calculations lead to inaccurate results. If in calculating a_1 according to a_2, the curve $\log \gamma_2 = \varphi(\log \gamma_1)$ is extrapolated to the origin of coordinates (see Fig. 156), then when computing a_2 (according to a_1) the curve asymptotically approaches the vertical axis (because upon dilution, i.e. an increase in the ratio x_1/x_2 to infinity, the quantity $\log a_1/x_1$ decreases to zero); this introduces considerable errors into graphical integration. This is why an artificial procedure was proposed, i.e. plotting a graph of a hypothetically selected function of a_1 that approaches zero upon dilution [A40].

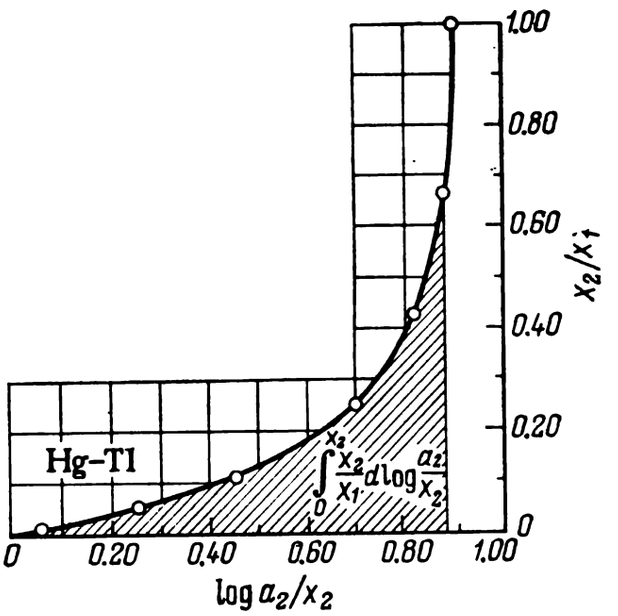


Fig. 156. Determining the activity of a solvent according to the dependence of the activity of the solute on the concentration. Thallium amalgam, $t = 25$ °C. (See Example 3)

When the solvent is volatile, the calculations are performed with the corresponding graph constructed on the basis of the equation

$$\int_{a_2'}^{a_2''} d \ln a_2 = -\int_{p_2'}^{p_1''} \frac{x_1}{x_2} d \ln \frac{p_1}{p_1^\circ} \qquad (12.13)$$

Example 3. Calculate the activity of mercury in thallium amalgams at 25 °C if the activity of thallium in amalgams of various concentrations at this temperature has the following values:

x_2 ...	0.01	0.05	0.1	0.2	0.3	0.4	0.5
a_2 ...	0.0115	0.090	0.284	0.996	1.98	3.03	3.99

Solution. We use Eq. (12.12) for the calculations. Accordingly, we compute the values of x_2/x_1 and $\log a_2/x_2$, and then construct a graph in the coordinates $x_2/x_1 = \varphi\,[\log (a_2/x_2)]$ on the basis of these data (see Fig. 156).

The area limited by the curve, the axis of abscissas and a perpendicular erected to the curve from the relevant point on the axis

of abscissas corresponds to the value of a_1/x_1. The intermediate calculations and the final results are given below :

x_2/x_1	0.0101	0.0526	0.111	0.250	0.429	0.666	1.000
$\log a_2/x_2$	0.061	0.255	0.453	0.697	0.820	0.879	0.902
$-\log a_1/x_1$	0.0005	0.0065	0.0220	0.0635	0.103	0.134	0.151
a_1	0.989	0.936	0.855	0.691	0.552	0.441	0.353

Calculations According to the Freezing Point Depression. By dividing Eq. (12.8) by dT, we get

$$\frac{d \ln a_2}{dT} = -\frac{x_1}{x_2}\frac{d \ln a_1}{dT} = -\frac{x_1}{x_2}\frac{\Delta H_f}{RT^2}$$

and for aqueous solutions

$$\frac{d \ln a_2}{dT} = -\frac{55.51}{m}\frac{\Delta H_f}{RT^2}$$

Since for dilute aqueous solutions the quantity $RT^2/55.51\ \Delta H_f = 1.858$ (p. 291), the latter relationship can be written down as follows :

$$d \ln a_2 = \frac{d(T^\circ - T)}{1.858m} = \frac{d\theta}{1.858m} \qquad (12.14)$$

In Eq. (12.14) $d\theta = d(T^\circ - T)$, where T° and T are the freezing points of the pure solvent and the solution, respectively. For convenience of integration, the quantity

$$j = 1 - \frac{\theta}{1.858m} \qquad (12.15)$$

is introduced [A40].

Let us differentiate Eq. (12.15). The relationship obtained in combination with Eq. (12.14) after transformation * and integration yields

$$-\ln \frac{a_2}{m} = \int_0^m j\, d \ln m + j \qquad (12.16)$$

---

* Indeed, rewriting Eq. (12.15) in the form

$$-j = \frac{\theta}{1.858m} - 1$$

we find that

$$-dj = \frac{d\theta}{1.858m} - \frac{\theta dm}{1.858m^2}$$

or

$$\frac{d\theta}{1.858m} = \frac{\theta}{1.858m} d \ln m - dj = (1 - j)\, d \ln m - dj$$

or

$$d \ln a_2 = d \ln m - j\, d \ln m - dj$$

Equation (12.16) is sufficiently accurate up to $m = 5$; the integral is taken according to a graph of $j/m = \varphi(m)$ (Fig. 157).

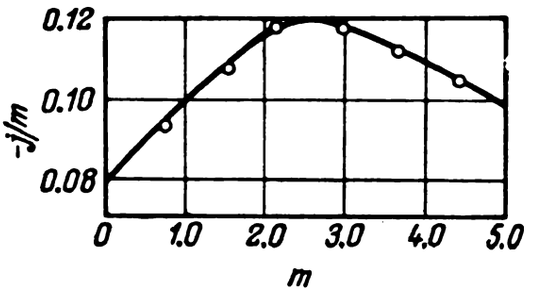


Fig. 157. Determining the activity of a solute according to the depression of the freezing point of the solution. Aqueous solution of cane sugar. (See Example 4)

For very dilute solutions, the ratio j/m may be considered approximately constant, and Eq. (12.16) becomes

$$\ln \frac{a_2}{m} = -2j \qquad (12.17)$$

The activity can be calculated according to the elevation of the boiling point in a similar way, but with less accuracy.

Example 4. Using the values of the lowering of the freezing point for aqueous solutions of cane sugar given below, calculate the activity coefficients of sugar for the indicated concentrations:

m	0.800	1.574	2.114	2.922	3.572	4.384
θ	1.60	3.42	4.91	7.31	9.32	11.98

Solution. First we calculate the values of j by Eq. (12.15). Next we determine the ratio j/m and in accordance with Eq. (12.16) plot a graph in the coordinates $j/m = \varphi(m)$ (see Fig. 157). According to this graph, we calculate $\int_0^m j\, d \ln m$, and then $\log \gamma_2$ and $\gamma_2 = a_2/m$.

The results of all the intermediate calculations and the final results are given below:

m	0.800	1.574	2.114	2.922	3.572	4.384
$-j$	0.076	0.169	0.250	0.346	0.404	0.469
$-j/m$	0.095	0.107	0.118	0.118	0.113	0.107
$\int_0^m j\, d \ln m$	0.070	0.147	0.210	0.304	0.353	0.444
$\log \gamma_2$	0.0647	0.137	0.200	0.282	0.329	0.397
γ_2	1.161	1.357	1.585	1.915	2.133	2.495

12.2.2. Electrolytes

The activity and activity coefficients of electrolytes are calculated by the same methods as for non-electrolytes. A brief review of all the methods is given below, except for the calculation according to the change in the solubility of a salt in the presence of other salts, treated on p. 425, and the method of the e.m.f., which has been included in Chap. 14 in connection with the calculation of equilibrium in electrochemical systems (Sec. 14.2.4).

The partition coefficient is used to determine the activity when an electrolyte is distributed between two liquids, in one of which the substances do not dissociate. Calculation of the activity according to the vapour pressure of the solute is limited to the few cases when the molecules of the electrolyte have a considerable volatility (such compounds include, for example, the hydrohalides).

In both cases if experimental data are available [in the first case $c_2 = \varphi(c_1)$, in the second $p = \varphi(m)$], the calculations can be carried out if extrapolation to infinite dilution is possible, because we get (for a mono-monovalent electrolyte)

$$\frac{\sqrt{c_2}}{c_1} = K'\gamma_1 \quad \text{and} \quad \frac{a_\pm}{m} = \frac{\sqrt{a_2}}{m} = \frac{\sqrt{p}}{m} = K\gamma$$

the proportionality factors of which equal $\sqrt{c_2}/c_1$ and $\sqrt{p}/m$ (at $m = m^*$, when $\gamma = 1$).

It is good to determine the activity according to the saturated vapour pressure of the solvent for concentrated solutions, because for dilute solutions this method gives results inferior in accuracy, particularly to the quite reliable method of calculations according to the freezing point depression of solutions.

The latter method for electrolytes is modified as follows. Equation (12.14) in accordance with Eq. (12.4) becomes

$$d \ln \gamma_\pm = -\frac{dT}{1.858\, m} - d \ln m \qquad (12.18)$$

To facilitate integration of Eq. (12.18), the empirical function

$$j = \frac{a}{1.858\nu} m^b \qquad (12.19)$$

was introduced [A40]. It gives a definite value upon extrapolation to infinite dilution. The coefficients of Eq. (12.19) are determined from the graph

$$\log\left(1.858\nu - \frac{\theta}{m}\right) = \varphi(\log m)$$

[where θ is the freezing point depression (Fig. 158)], since when Eq. (12.15) written down for an electrolyte is combined with Eq. (12.19), it follows that

$$1.858\nu - \frac{\theta}{m} = am^b$$

Combining Eq. (12.16) written down in the differential form with Eq. (12.19), we get *

$$\log \gamma_\pm = -\frac{a(1+b)}{4.279\nu b} m^b \qquad (12.20)$$

or for a given electrolyte

$$\log \gamma_\pm = -Cm^b \qquad (12.21)$$

where $C = a(1+b)/4.279\nu b$. The results of the calculations are accurate up to $m = 0.01$ to 0.05 within a temperature interval of ± 15 kelvins, when $a_2 \neq \varphi(T)$.

Appendix 10 gives the values of the activity coefficients for selected electrolytes in aqueous solutions at 25 °C. More complete tables of the values of γ (also covering high concentrations) are given in [B71].

Expansion of Eq. (12.20) into a series gives (for $b \doteq 0.5$)

$$\gamma_\pm = 1 - \frac{3a\sqrt{m}}{1.858\nu} + \frac{1}{2}\left(\frac{3a\sqrt{m}}{1.858\nu}\right)^2 + \cdots$$

Disregarding all the terms of the expansion except the first two for very dilute solutions, in accordance with Eq. (12.19) we get

$$\gamma = 1 - 3j \qquad (12.22)$$

To calculate the activity coefficient for concentrated solutions, when we can no longer ignore the heat of dilution and its temperature dependence, we must know the partial molar heat capacities and the enthalpies.

Calculations show that for mono-monovalent electrolytes $b \approx 0.5$, i.e.

$$j = \frac{a\sqrt{m}}{1.858\nu} \qquad (12.23)$$

---

* Indeed,

$$d \ln \gamma = j\, d \ln m - dj = (a/1.858\nu)\, m^{b-1}\, dm - (a/1.858\nu)\, d(m^b)$$

therefore

$$\ln \gamma = -(a/1.858\nu)\,(m^b/b) - (a/1.858\nu)\, m^b$$

(since the integration constant equals zero); from the last equation it follows that

$$\ln \gamma = -(a/1.858\nu)\,(1/b + 1)\, m^b$$

and from Eqs. (12.20) and (12.22)

$$\ln \gamma_{\pm} = -\frac{3a\sqrt{m}}{1.858\nu} = -3j \qquad (12.24)$$

Example 5. Aqueous solutions of Na_2SO_4 have the following freezing points:

m	0.003 527 2	0.008 603 0	0.016 155	0.032 064	1.103 38
$-t_{fr}$	0.018 382	0.043 557	0.079 371	0.151 60	0.450 22

Calculate the activity coefficients of Na_2SO_4 for $m = 0.001$, 0.002, 0.005 and 0.01.

Solution. To find the coefficients a and b in Eq. (12.20), we use Eq. (12.19) to plot a graph in the coordinates $\log (1.858\nu - \theta/m) = \varphi(\log m)$ (see Fig. 158). The graph gives us $b = 0.3846$ and $a = \text{antilog } 0.50 \approx 3.16$.

Consequently, Eq. (12.20) has the form

$$\log \gamma_{\pm} = -\frac{3.16(1 + 0.3846)}{4.279 \times 3 \times 0.3846} m^{0.3846} = -0.889 m^{0.3846}$$

Using in this equation the values of m given in the initial conditions of the example, we get

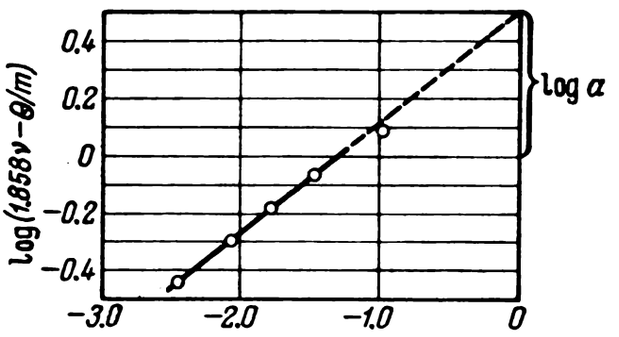


Fig. 158. Determining the activity of a solute according to the depression of the freezing point of an electrolyte solution.
Aqueous solution of Na_2SO_4. (See Example 5)

m ...	0.001	0.002	0.005	0.01
$\gamma_{\pm}$ ...	0.87	0.83	0.76	0.69

The method of similarity (dimensionless parameters) can also be used for an approximate assessment of the activity coefficient. The transition from the relationship $\gamma = \varphi(m)$ to $\gamma/\gamma_{min} = \varphi(m/m_{\gamma min})$ results in the curves approaching one another, and for systems containing substances that are analogues, in their actual merging. An example is shown in Fig. 159. The centre of the figure also contains a graph of $\gamma_{min} = \varphi(m_{\gamma min})$ for the same substances (it corresponds to the second method of comparative calculations [B45]). Such relationships can be helpful in predicting the properties of insufficiently studied systems. Assume, for instance, that in the series of aqueous solutions of alkali metal chlorides γ_{min} and $m_{\gamma min}$ in a

first approximation are a linear function of the radius of a cation. For a solution of FrCl this gives $m_{\gamma_{min}} \approx 4.7$ and $\gamma_{min} \approx 0.45$, whence Fig. 159 permits us to easily find the relationship $\gamma = \varphi(m)$ for this solution without having any experimental data at our disposal.

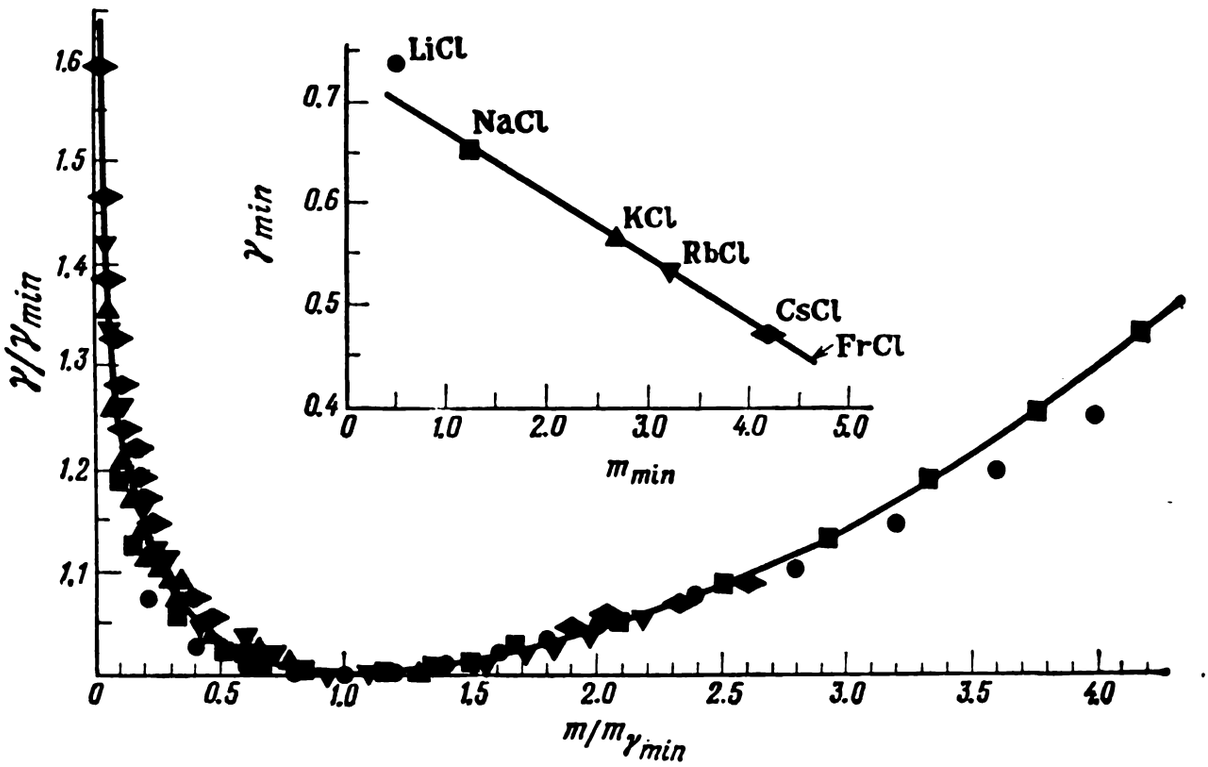


Fig. 159. Dependence of the activity coefficient of aqueous solutions of alkali metal chlorides on their molality at 25 °C in a reduced system of coordinates

Ionic Strength Rule. Unlike a change in temperature, a change in concentration appreciably affects the values of the activity coefficients. For weak electrolytes, we can assume that $\gamma_i = \alpha_i$ and thus relate the decrease in the activity coefficients when the concentration grows to a drop in the degree of dissociation. At considerable concentrations, and for strong electrolytes at all concentrations, such an explanation is absolutely unsatisfactory (all this is illustrated by Fig. 153).

The solution of the problem should be sought in the electrical nature of the interaction between ions. The deviations are explained not by incomplete dissociation, but by electrostatic effects.

An empirical formula was proposed that relates the activity coefficient to the concentration of the ions of a given species, their

valence and the relative permittivity (dielectric constant) of the solvent:

$$-\log \gamma_i = \frac{26 z_i \sqrt[3]{c_i}}{D} \tag{12.25}$$

Somewhat later, a rule known as the **ionic strength rule,** especially important in studying mixtures of electrolytes, was established. This rule states that *the activity coefficient of a given strong electrolyte is the same in all solutions having an equal ionic strength.* By **ionic strength** I here is meant the half-sum of the products of the molalities of all the ions and the squares of their valence *, i.e. the quantity

$$I = \frac{1}{2} \sum m z_i^2 \tag{12.26}$$

It follows from the ionic strength rule that in a solution of strong electrolytes of the same valence type, the activity coefficient of each depends only on the total concentration.

It must be stressed that, strictly speaking, this law may be applied only to infinitely dilute solutions, and its use in practice is limited to dilute solutions (up to about $0.2N$).

It would be possible to calculate the activity coefficients of separate ions according to that of a salt including them if the activity coefficient of the second ion is known. It is generally assumed for these calculations that the activity coefficients of the ions Cl^- and K^+, which have an approximately identical mobility, are equal (for $m = 0.01$ we have $\gamma_{K+} = \gamma_{Cl-} = 0.922$). Hence, assuming that the activity coefficient of a separate ion depends only on the ionic strength of the solution, we can, by passing over from one electrolyte to another (with a common ion), calculate the activity coefficients of the separate ions. Because of a certain arbitrariness of the initial data and the impossibility of extending the ionic strength rule to any concentrations, such calculations cannot give accurate results, although for practical purposes it is very convenient to consider that the activity coefficients of ions of the same valence are approximately equal if the ionic strengths of the solutions are identical.

Generalized values of the activity coefficients are given below:

I	0.001	0.01	0.02	0.05	0.10
γ, monovalent ions	0.98	0.92	0.89	0.85	0.80
γ, bivalent ions	0.77	0.58	0.50	0.40	0.30

* Sometimes by the ionic strength we mean the quantity $\sum m z_i^2$.

Activity Coefficients in Mixtures of Electrolytes and Solubility. Since the activity of a solid salt equals its activity in a saturated solution, and the latter at p, T = const is also constant, it follows from Eq. (12.4) that the activity coefficient of a salt should change inversely proportional to the mean molality of its ions. If we use data on the solubility of a salt being studied in the presence of other salts to plot a graph in the coordinates $m_{\pm}^{-1}$ against $\sqrt{I}$ (Fig. 160), we can easily find the limiting value $1/m_{\pm}^{*}$ by extrapolation of the curve up to its intersection with the axis of ordinates. By dividing any of the experimentally found values of $m_{\pm}^{-1}$ by the found value, we shall get the activity coefficient corresponding to the given concentration.* This method of calculation is very accurate. It can also be used to solve the reverse problem — determine the solubility of a poorly soluble salt in the presence of other salts. It is easy to show that the solubility of a poorly soluble salt lowers in the presence of salts containing common ions, whereas in the presence of salts not containing such ions it grows in comparison with the solubility in pure water.

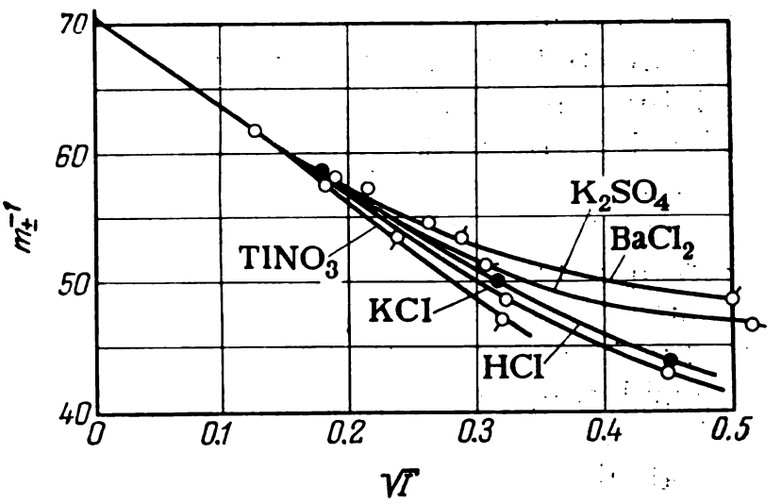


Fig. 160. Determining the activity coefficients from the solubility of salts in solutions of electrolytes.
TlCl in water in the presence of other salts, t=25 °C. (See Example 6)

Example 6. Use the following data to determine the activity coefficient of TlCl in a 0.025M aqueous solution of KCl. (The solubility of TlCl in this solution at 25 °C is 0.008 69 mol/dm³.)

c_{KCl}, M	0.0	0.025	0.05	0.1	0.2
c_{TlCl}, mol/dm³	0.016 07	0.008 69	0.005 90	0.003 96	0.002 68

Solution. For $m_{KCl} = 0.025$ we have $m_{TlCl} = 0.008\ 69$, therefore $m_+ = 0.008\ 69$, while $m_- = 0.025 + 0.008\ 69 = 0.033\ 69$, and $m_{\pm} = (0.008\ 69 \times 0.033\ 69)^{\frac{1}{2}} = 0.017\ 11$. Consequently, $m_{\pm}^{-1} = 58.4$.

* Why $\sqrt{I}$ instead of I is plotted along the axis of abscissas will be seen below. Meanwhile, this choice is motivated by the convenience of extrapolation, because for low concentrations ($I \to 0$) the curve becomes a straight line. This had been discovered empirically, and later was substantiated theoretically (see below).

Conducting similar calculations for other concentrations and determining the value of I for them from Eq. (12.26), we plot a graph in the coordinates $m_{\pm}^{-1}$ against $\sqrt{I}$ (see Fig. 160), and by extrapolation determine $(m_{\pm}^{-1})^* = 70.3$. Next we find

$$(\gamma_{\pm})_{m_{KCl}=0.025} = \frac{58.4}{70.3} = 0.831$$

Debye-Hückel Equation. The concept of activity and the activity coefficient as well as that of purely empirical functions was substantiated in the theory of strong electrolytes developed by P. Debye, E. Hückel (1923) and others.

The derivation of the formula for calculating the activity coefficients of electrolytes is based on the postulate of complete dissociation and the corresponding assumption that all the anomalies in the properties of solutions of strong electrolytes (in the osmotic pressure, saturated vapour pressure, electric conductivity, etc.) are due to electrostatic forces acting between the ions.

Considering each ion as a centre around which other ions group in the form, as it were, of a diffuse layer (ionic atmosphere), we can calculate the electric potential of the ion with respect to the solution surrounding it. Next determining the work done to remove the ions from one another in the process of dilution of the solutions, we can use the relationship between the activity and the change in the Gibbs energy to find an equation for calculating the activity coefficient for each species of ions:

$$-\log \gamma_{\pm} = \frac{z_i^2 e^3 \sqrt{2\pi N_A/1000}}{2.303(DkT)^{\frac{3}{2}}} \sqrt{m_i z_i^2} \qquad (12.27)$$

where e = charge of an electron
N_A = Avogadro constant
D = relative permittivity of the medium
k = Boltzmann constant.

By combining all the constant quantities of Eq. (12.27) and taking into account Eq. (12.3), we can write down Eq. (12.27) for the mean activity coefficient * in the form

$$-\log \gamma_{\pm} = z_+ z_- A \sqrt{I} \qquad (12.28)$$

where $A = \frac{e^3 \sqrt{2\pi N_A/1000}}{2.303(Dk)^{\frac{3}{2}}}$ (here e is the charge of an electron).

Consequently, at equal ionic strengths, electrolytes should have identical activity coefficients. This is how the ionic strength rule is substantiated (see p. 424).

* In accordance with the fact that $\log \gamma_{\pm} = (1/\nu)(\nu_+ \log \gamma_+ + \nu_- \log \gamma_-)$ and he obvious equality $\nu_+ z_+ = \nu_- z_-$.

For aqueous solutions at 25 °C, the coefficient $A = 0.5085$, therefore Eq. (12.28) becomes:

for mono-monovalent electrolytes for which by Eq. (12.26) we have $I = m$

$$-\log \gamma_{\pm} \approx 0.5 \sqrt{m} \tag{12.29}$$

for mono-bivalent electrolytes for which $z_+z_- = 2$ and $I = 3m$

$$-\log \gamma_{\pm} \approx 1.0 \sqrt{3m} \tag{12.30}$$

for mono-trivalent electrolytes for which $z_+z_- = 3$ and $I = 6m$

$$-\log \gamma_{\pm} \approx 1.5 \sqrt{6m} \tag{12.31}$$

etc. These equations summarize experimental data quite well (Fig. 161). At moderate and high concentrations, however, the linear relationship $\log \gamma_{\pm} = \varphi(\sqrt{I})$ is violated. The impossibility of using the ionic strength rule for considerable concentrations of solutions is explained not so much by mathematical simplifications as by the assumptions made when deriving Eq. (12.27) (the assumptions that ions are point charges, that the formation of an ionic atmosphere around a given ion is independent of the formation of an ionic atmosphere around other ions, and that the influence of the solvent can be taken into account completely by introducing its relative permittivity). These assumptions hold only for very dilute solutions. The following equation was obtained after introducing a correction for the size of the ions:

$$-\log \gamma_{\pm} = \frac{z_+z_-A\sqrt{I}}{1 + a_0B\sqrt{I}} \tag{12.32}$$

in which the coefficient B combines several constants, while the coefficient A has the same value as in Eq. (12.28). The values of these coefficients for aqueous solutions are given in Table 12.

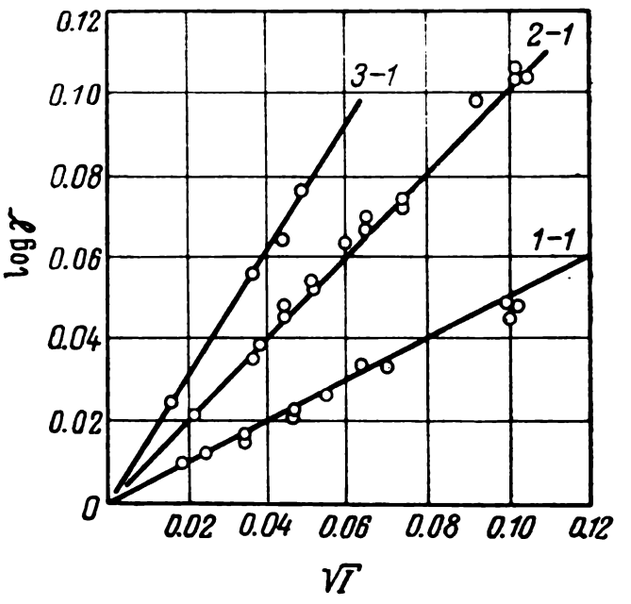


Fig. 161. Dependence of activity coefficients on the ionic strength found from the solubility of various kinds of salts in solutions of different electrolytes.

Checking of Eq. (12.28)

The quantity a_0 in Eq. (12.32) can be assumed approximately equal to the size of the ions, approximately not because it changes from one ion to another, but because Eq. (12.32) takes into account only one error among many. Therefore the introduction of the radius of an ion into it cannot produce accurate results,

although in a first approximation the quantity a_0 can be considered equal to the mean distance up to which every ion can approach any other one ($a_0 = 2 \times 10^{-8}$ to 5×10^{-8}).

Table 12. **Coefficients A and B of Eq. (12.32) for Aqueous Solutions**

t	A	$B \times 10^{-8}$	t	A	$B \times 10^{-8}$	t	A	$B \times 10^{-8}$
0	0.4883	0.3241	35	0.5175	0.3297	70	0.5537	0.3354
5	0.4921	0.3249	40	0.5221	0.3305	75	0.5596	0.3363
10	0.4960	0.3258	45	0.5279	0.3314	80	0.5638	0.3372
15	0.5000	0.3266	50	0.5319	0.3321	85	0.5722	0.3380
20	0.5040	0.3273	55	0.5371	0.3329	90	0.5788	0.3390
25	0.5085	0.3281	60	0.5425	0.3338	95	0.5857	0.3399
30	0.5130	0.3290	65	0.5480	0.3346	100	0.5929	0.3409

Hückel took into consideration the changes in the relative permittivity near an ion and derived a more accurate equation which differs from Eq. (12.32) by having an additional term proportional to the ionic strength (with the minus sign). The proportionality factor is determined by inserting experimental data into this equation.

For non-electrolytes in the presence of an electrolyte, the equation

$$\log \gamma = CI \qquad (12.33)$$

may be used. Here the coefficient C depends on the nature of the electrolyte ions and is determined experimentally. It follows from Eq. (12.33) that the freezing out of a substance from a solution increases with a growth in the ionic strength; consequently, the solubility of a substance in the presence of an electrolyte lowers (the salting-out effect).

Example 7. Using Eq. (12.32), find according to the solubility of $Ca(OH)_2$ in water at 30 °C ($m = 0.0202$) its activity coefficient in a saturated solution.

Solution. From Eq. (12.26), we find the ionic strength of $Ca(OH)_2$ in a saturated solution: $I = \frac{1}{2}(1 \times 0.0202 \times 2^2 + 2 \times 0.0202 \times \times 1^2) = 0.0606$.

Assuming that $a_0 = 4 \times 10^{-8}$, we use the data of Table 12 and Eq. (12.32) to get

$$-\log \gamma_{\pm} = \frac{2 \times 1 \times 0.513\sqrt{0.0606}}{1 + 4 \times 10^{-8} \times 0.329 \times 10^{8}\sqrt{0.0606}} = 0.1908$$

and

$$\gamma_{\pm} = 0.64$$

Chapter 13

CHEMICAL EQUILIBRIUM CONSTANT AND CHANGE IN GIBBS ENERGY*

13.1. INTRODUCTION

The first attempts (at the beginning of the 18th century) to assess quantitatively the ability of various substances to enter into a chemical reaction were based on the notion of a definite relationship between the force of "chemical affinity" and the state and composition of substances. These attempts resulted in systematization of the material in "affinity tables" presenting first the mutual sequence of the affinity of substances, and later quantitative relationships. As data accumulated, many exceptions to these tables were discovered. Therefore their very idea was cast in doubt, particularly by C. Berthollet, who introduced the concept of chemical equilibrium and the assumption that the course of a reaction also depends on the amount of the reactants. Berthollet erroneously negated the constancy of the composition of chemical compounds, however, by including solutions among them. This error was apparently the reason why Berthollet's correct ideas remained unacknowledged for a long time; they were further developed only in the 1860's.

As a result of the investigations of N. Beketov (1865), C. Guldberg and the chemist P. Waage (1867), the idea was confirmed that chemical action depends on the concentration of the reactants. The **law of mass action** was established, and thus Berthollet's ideas were given a mathematical form — the reversibility of a chemical reaction received a quantitative expression.

What is really the measure of affinity?

H. Thomson (1853) and M. Berthelot (1867) suggested measuring chemical affinity by the amount of heat liberated in a reaction. Berthelot later turned this idea into a principle **(Berthelot's principle)** according to which chemical reactions proceed spontaneously in the direction of the liberation of heat.

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* It is recommended to repeat the material of Chap. 5, especially Secs. 5.1, 5.2 and 5.4, before studying this chapter.

With the accumulation of experimental data, it was discovered that Berthelot's principle was not correct in its general form. First, the fact that an enormous number of spontaneous endothermic processes are known had to be taken into consideration. Second, N. Beketov established (1865) that the same reactions proceeding in one set of conditions with the liberation of heat, i.e. in accordance with Berthelot's principle, in other conditions proceed with the absorption of heat.

A significant role in determining the limitations in the application of Berthelot's principle was played by D. Mendeleev (1875) and especially by A. Potylitsyn (1874), who in a number of studies proved the truth of this principle only as a limiting law at $T = 0$. Beketov also pointed to this circumstance in his "Physicochemistry" (1886). *

J. Gibbs (1878) and H. Helmholtz (1884) laid the foundation of the modern theory of chemical affinity. J. van't Hoff (1885) developed it and imparted a mathematical form to it, giving a thermodynamic derivation of the law of mass action.

Chemical affinity is measured by the work that can be obtained when a given process is conducted in the reverse direction, i.e. by the change in a thermodynamic potential. As applied to processes at p, T = const, this means that *affinity is measured by the change in the Gibbs energy*. Indeed: (1) the value of ΔG depends not on the path of a process, but on the properties of the reagents and their state; (2) the sign of ΔG is determined by the direction of a process; and (3) in equilibrium G is minimum, i.e. spontaneous changes in a system are excluded.

Solving the problem of the true measure of affinity makes it possible to substantiate the procedure for measuring and calculating it and to correctly assess Berthelot's principle. The latter is also of great importance because it is much easier to determine ΔH than ΔG.

The difference between the true measure of affinity $(-\Delta G)$ and the measure of affinity according to Berthelot $(-\Delta H)$ is expressed by Eq. (5.22):

$$-\Delta G = -\Delta H + T\Delta S = -\Delta(H - TS)$$

As follows from this equation, Berthelot's principle is equivalent to the statement that work is done at the expense of a decrease in enthalpy. At constant pressure and temperature, however, this statement holds when applied to the decrease in the Gibbs energy.

* It must be noted that Berthelot's principle was anticipated by H. Hess (1839), who stated that "the stronger substances combine with each other, the greater is the amount of heat that should be liberated" and "the amount of liberated heat can serve as a measure of chemical affinity" (1842). Hess did not attach a categorical meaning to this postulate, however.

Similar reasoning can also be applied to Eq. (5.7).

The equation relating ΔG and ΔH shows that Berthelot's principle is strictly true in two *special* cases: (1) when $\Delta S = 0$, i.e. when in accordance with the equation $(\partial \Delta G/\partial T)_p = -\Delta S$ following from Eq. (5.24) the maximum useful work does not depend on temperature, and (2) when $T = 0$. The closer T is to absolute zero, the more accurately does the quantity ΔH express the quantity ΔG and the more probable is a direction of the process such that heat will be liberated.

In essence, it is sufficient for ΔS or T to have small values instead of equalling zero, since if $T\Delta S$ is small, the signs of ΔH and ΔG will coincide. Indeed, at very low temperatures, exothermic processes usually proceed spontaneously. Therefore, Berthelot's principle can serve as a simple and sufficiently reliable, at least in the first approximation, criterion of the possibility of a process at low temperatures, and it is especially reliable for reactions in condensed systems, where the value of ΔS is low.

Experimental data also indicate the correctness of this principle for moderate temperatures (especially for substances with a high temperature of decomposition). This is not unexpected, because the temperatures generally used should in essence be related to low ones. In addition, for chemical reactions the change in the entropy is often also small at moderate temperatures, and therefore $\Delta H \gg \gg T\Delta S$.

For spontaneously proceeding endothermic reactions and for exothermic reactions that cannot be carried out (in the given conditions), the values of ΔH and ΔG, however, already differ not only in their order of magnitude, but also in their sign. Thus, if the burning of graphite is an example of a process for which ΔG and ΔH at $p = 1$ atm coincide in sign and magnitude, then the reaction of formation of pentane from simple substances is an example when ΔG and ΔH differ both in sign and in magnitude; in the latter case $\Delta H < 0$ and $\Delta G > 0$, i.e. contrary to Berthelot's principle this reaction cannot be carried out.

Thus, it would be more correct to call Berthelot's principle, which he named the **principle of maximum work,** the *rule of maximum heat.* Notwithstanding all its shortcomings and its misleading name, it is undoubtedly impossible to negate the significance of Berthelot's principle. It was the first serious attempt to give a quantitative assessment of affinity and facilitated the accumulation of extensive experimental data that made it possible to establish a true measure of chemical affinity. Finally, the circumstance that reactions proceed practically without a change in entropy at very low temperatures (see pp. 461f) is also significant, i.e. Berthelot's principle does justify the name of the principle of maximum work. Thus, if

for the condition p = const, the condition S = const is observed, then the decrease in enthalpy in accordance with Eq. (5.4) equals the decrease in the Gibbs energy.

13.2. DETERMINING ΔG FROM THE E.M.F.

To find the change in the Gibbs energy, a reaction must be conducted reversibly and at constant pressure and temperature. It is most expedient to use the method of determining ΔG from the e.m.f. of a galvanic cell, because the process in it is the closest to a reversible one: the e.m.f. of the cell and the external e.m.f. can be accurately balanced.

After measuring the maximum e.m.f. of a cell by the potentiometric method, we can determine ΔG of the reaction by the equation

$$\Delta G = -zFE_{max} = -23\,062zE_{max} \qquad (13.1)$$

(the subscript "max" will be omitted in the following).

The signs adopted in Eq. (13.1) correspond to the condition of the spontaneous nature of the process at $E > 0$. The equation of an electrochemical reaction should correspond to the condition that in operation of a cell the anions within it move from the right to the left, and the electrons in the external circuit from the left to the right.

Because of the impossibility of determining the absolute potential of an electrode, a hydrogen electrode immersed in a solution containing hydrogen ions with an activity equal to unity is taken as the conventional zero-electrode. In accordance with the adopted rule of signs, an electrode having greater oxidizing properties than hydrogen is positive.

Combining Eqs. (13.1) and (5.26), we get

$$\Delta G = -23\,062zE = \Delta H - 23\,062zT\left(\frac{\partial E}{\partial T}\right)_p$$

whence

$$E = -\frac{\Delta H}{23\,062z} + T\left(\frac{\partial E}{\partial T}\right)_p \qquad (13.2)$$

This equation expresses the relationship between the electric energy of a reversibly operating cell (at p, T = const) and the heat effect of the current-forming process.

The relationship between ΔG and ΔH is determined by the sign of the temperature coefficient of the cell e.m.f. The following cases are possible (Fig. 162):

1. The temperature coefficient of the e.m.f. $(\partial E/\partial T)_p = 0$ (line *1*). Here $-\Delta G = W'_{max} = -\Delta H$, i.e. work is done at the expense of a decrease in enthalpy, therefore the cell operates without heat exchange. Processes for which $\Delta H = 0$ ($E = 0$) or $\Delta H > 0$ ($E < 0$) cannot occur. This case corresponds to the **Thomson rule** (1847),

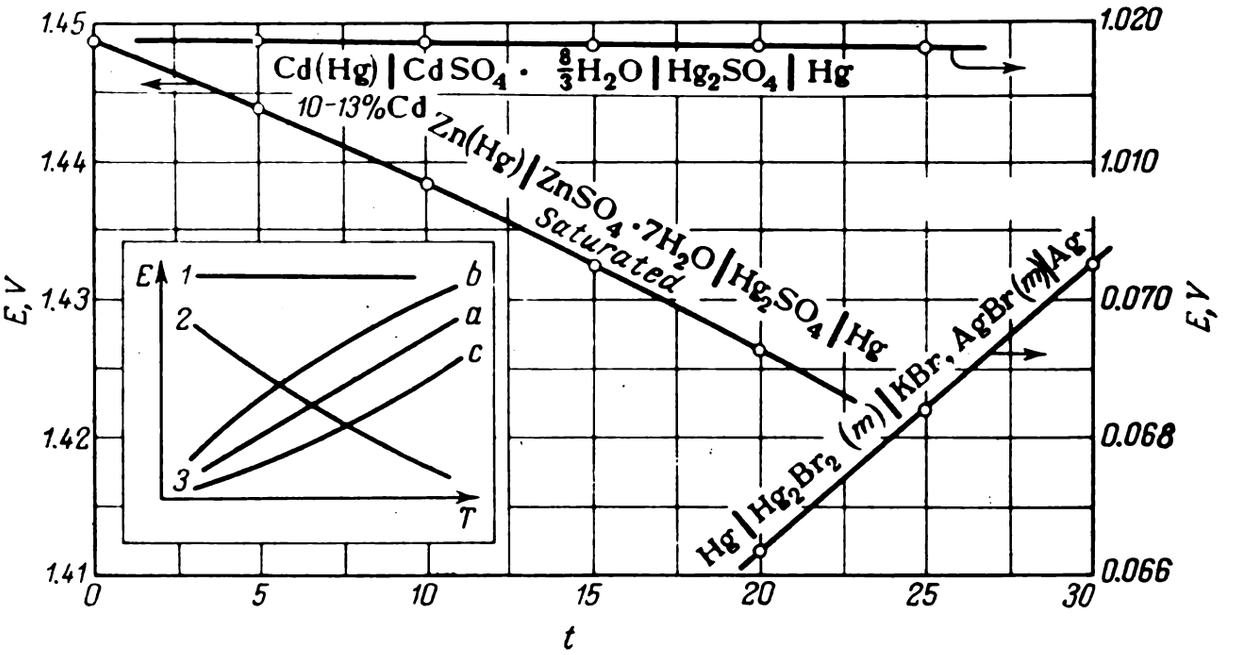


Fig. 162. Temperature dependence of e.m.f.
Illustrating the calculation of the change in the Gibbs energy. (See Example 2)

established on the basis of the law of conservation of energy. It is quite clear that the Thomson rule is the result of applying Berthelot's principle to electrochemical processes. Like this principle, it holds not only when $\Delta S = 0$, i.e. when $(\partial E/\partial T)_p = 0$, but also when $T \to 0$.

2. The value of $(\partial E/\partial T)_p < 0$ (curve *2*). Here $-\Delta G(W'_{max}) < -\Delta H$, i.e. the work is less than the heat effect of the corresponding chemical process. Processes are excluded for which $\Delta H < 0$ ($E < 0$). The cell gives up the surplus energy to the surroundings, i.e. only part of the chemical energy transforms into electric energy. If it is impossible to remove heat from a cell, the latter will become heated. Strictly speaking, it should heat infinitely slowly, otherwise the process will become irreversible, i.e. the condition of applying Eq. (5.26) will be violated. This case is encountered more often than the others.

3. The value of $(\partial E/\partial T)_p > 0$ (curves *3*). Here $-\Delta G(W'_{max}) > -\Delta H$, i.e. the work of the electric current is greater than the heat effect of the reaction. Therefore, heat is taken from the surroundings, and in adiabatic conditions the cell cools infinitely slowly.

In the last case, the nature of the change in E with T must be taken into consideration:

(a) if the temperature dependence of E is a straight line (line *3a*), i.e. $(\partial E/\partial T)_p = \text{const}$ or $(\partial E/\partial T)_p = (E/T)_p$, then $T(\partial E/\partial T)_p = E$, and from Eq. (13.2) we have $\Delta H = 0$. This means that work is done only at the expense of heat from the surroundings;

(b) if the temperature coefficient diminishes with increasing temperature, i.e. $(\partial E/\partial T)_p < (E/T)_p$, then $T(\partial E/\partial T)_p < E$, and hence $\Delta H < 0$ (curve *3b*), i.e. work is partly done as a result of the absorption of heat from the surroundings;

(c) if the temperature coefficient grows with increasing temperature (curve *3c*), i.e. $(\partial E/\partial T)_p > (E/T)_p$, then $T(\partial E/\partial T)_p > E$, and hence $\Delta H > 0$, i.e. part of the absorbed heat is used to do work and part goes to increase the enthalpy of the system. Here it is essential that the second term of the right-hand side of Eq. (13.2) be greater than the first in absolute value (low values of ΔH, high values of T).

The relationship between E and $T(\partial E/\partial T)_p$ for case 2 is always the same, because $(\partial E/\partial T)_p < 0$, while $(E/T)_p > 0$.

The above cases could also be analysed proceeding from the influence of the sign of ΔH on the nature of the change in E with the temperature, i.e. on the basis of Le Chatelier's principle (see Sec. 5.4.3).

It should be noted that in the absence of phase transitions within the temperature interval being studied, as a rule $\partial E/\partial T$ is approximately constant. If the temperature coefficient of the e.m.f. is strictly constant, then $\Delta C_p = 0$. Indeed, in this case $\partial^2 \Delta G/\partial T^2 = 0$ and by Eq. (5.26)

$$\frac{\partial \Delta G}{\partial T} = \frac{\partial \Delta H}{\partial T} + T\frac{\partial^2 \Delta G}{\partial T^2} + \frac{\partial \Delta G}{\partial T} = 0$$

i.e.

$$\frac{\partial \Delta H}{\partial T} = 0$$

Should a phase transition (for example melting of one of the electrodes) occur within the temperature interval being studied, then at a constant e.m.f. ($-zF\Delta E_{\text{ph.tr}} = \Delta G_{\text{ph.tr}} = 0$) the quantity $\partial E/\partial T$ will change stepwise at this point, because

$$\frac{23\,062z\partial E}{\partial T} = \left(\frac{\partial \Delta G}{\partial T}\right)_{\text{ph.tr}} = -\Delta S_{\text{ph.tr}} \neq 0$$

A step in $(\partial E/\partial T)_{\text{ph.tr}}$ can be used to determine $\Delta H_{\text{ph.tr}}$: since $E_{T_{\text{ph.tr}}+dT} = E_{T_{\text{ph.tr}}-dT}$, by Eq. (13.2) we have

$$-\frac{\Delta H_{T_{\text{ph.tr}}+dT}}{23\,062z} + T_{\text{ph.tr}}\frac{\partial E_{T_{\text{ph.tr}}+dT}}{\partial T} = -\frac{\Delta H_{T_{\text{ph.tr}}-dT}}{23\,062z} + T_{\text{ph.tr}}\frac{\partial E_{T_{\text{ph.tr}}-dT}}{\partial T},$$

or

$$\frac{T_{\text{ph.tr}}\partial\Delta E}{\partial T} = -\frac{\Delta H_{\text{ph.tr}}}{23\,062z}$$

whence

$$\Delta H_{\text{ph.tr}} = -\frac{23\,062zT\partial\Delta E}{\partial T}$$

The above method of calculating ΔG is mainly used for inorganic reactions. In organic chemistry, it can be used for a comparatively small number of oxidation-reduction processes. It cannot therefore be considered as one of the general methods of calculating equilibrium.

Attention should be given to an urgent problem arising from the possibility of conducting a reaction in a galvanic cell, namely, to the problem of converting the chemical energy of fuel directly (without its intermediate conversion into heat) into electric energy. Thus, calculations show that a reversible carbon-oxygen cell, i.e. a cell in which the reaction $C + O_2 = CO_2$ would proceed, would make it possible to convert 99.78% of the energy of combustion into useful work ($\Delta G \approx \Delta H$). The theoretical possibility of bringing the coefficient of fuel utilization up to high values is attracting great attention to the problem of creating a fuel cell.

The heat effect of a reaction can be found in addition to ΔG by conducting a reaction in a galvanic cell. It follows from Eq. (13.2) that for this purpose we must have at our disposal the temperature dependence of the e.m.f. within the corresponding temperature interval. For these calculations, we can resort to a graph of E against T, from which it is a simple matter to find the values of E and $(\partial E/\partial T)_p$ needed to calculate ΔH. The results of such calculations are distinguished by their great accuracy, because an electrochemical reaction can actually be a reversible process, and electrochemical measurements are more accurate (and simpler) than calorimetric ones.

An analysis of Eq. (13.2) shows that the difference between the sums of the values of the heat of formation and solution of like compounds of two elements is a constant quantity for all the com-

pounds of these elements (at T = const). This rule, which permits us to assess the values of the heat of formation and solution for similar compounds (for example for salts of two metals) was established by N. Khomutov (1940).

Example 1. Analyse the process in a lead-acid accumulator thermodynamically and find $(\partial E/\partial T)_p$ if $E_{298} = 2.03$ V.

Solution. If we place a sulphuric acid solution, lead and lead dioxide in a calorimeter under a constant pressure, then the following irreversible process will occur:

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O$$

It is attended by the liberation of 121.41 kcal (see Appendix 2). But the same substances can be used to construct a galvanic cell. Let us immerse it into a thermostat at 25 °C and form a short circuit. Now 60 705 cal will be liberated per gramme-atom of reacted lead. If the cell operates in conditions of compensation, its e.m.f. will be 2.03 V. Hence, discharging the accumulator reversibly, we shall get work equal to $2 \times 23\,062 \times 2.03 \approx 94\,600$ cal.

From Eqs. (5.22) and (12.2) we have

$$T\Delta S = 23\,062 \times 2 \times 298.2\left(\frac{\partial E}{\partial T}\right)_p = 33\,895$$

This value is the heat absorbed by the reacting substances (per gramme-atom of lead) from the surroundings upon the reversible isothermal and isobaric discharge of the accumulator. If discharging proceeds adiabatically, the accumulator will cool. Thus in the given case, the heat effects of the irreversible (−60 705) and reversible (+33 895 cal) processes differ not only in magnitude, but also in sign.

It follows from the last relationship that

$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{33\,895}{23\,062 \times 2 \times 298.2} \approx 0.002\,464 \text{ V/K}$$

Example 2. Find the standard heat effect of the reaction

$$\frac{1}{2}H_2 + \frac{1}{2}Hg_2Cl_2 = HCl(0.1m) + Hg$$

if for the cell $Pt(H_2) \mid HCl\ (0.1m) \mid \frac{1}{2}Hg_2Cl_2 \mid Hg$ we have $E = 0.399\,46$ V and $(\partial E/\partial T)_p = 0.000\,115$. Compare the result obtained with the calorimetric value of $\Delta H_{291} \approx -8000$ cal/mol.

Solution. Inserting into Eq. (13.2) the values of $E = 0.399\,46$, $z = 1$, $T = 298.2$ and $(\partial E/\partial T)_p = 0.000\,115$, we get

$$\Delta H_{298} = 23\,062 \times 1 \times 298.2 \times 0.000\,115 - 23\,062 \times 1 \times$$
$$\times\, 0.399\,46 = -8420 \text{ cal/mol}$$

The very great (negative) value of $(\bar{C}_p)_{HCl}$ (see Fig. 73, p. 265) results in a considerable absolute value of ΔC_p, and therefore in accordance with Eq. (3.26) the temperature coefficient of ΔH for this reaction is very high. Consequently, conversion is needed from $T = 298.2$ to $T = 291.2$ K. Since

$$\Delta H_{291} \approx \Delta H_{298} + \Delta C_p(291.2 - 298.2)$$

then, taking from Appendix 2 the values of the heat capacities of H_2, Hg_2Cl_2 and Hg and determining from Fig. 73 the heat capacity of HCl (0.1*m*), we get

$$\Delta H_{291} \approx -8420 + \Big[(-29.3 + 6.69) - \Big(\frac{1}{2} \times 6.89 + \frac{1}{2} \times$$
$$\times\, 23.88\Big)\Big](-7) \approx -8153 \text{ cal/mol}$$

This value differs from that found calorimetrically by 1.3%.

13.3. RELATIONSHIP BETWEEN CHANGE IN GIBBS ENERGY AND EQUILIBRIUM CONSTANT

The most important and general method for calculating the change in the Gibbs energy is its determination from *data on chemical equilibrium.*

If at p, $T = \text{const}$ the reaction

$$b\text{B} + c\text{C} + \ldots = r\text{R} + s\text{S} + \ldots$$

proceeds, the change in the Gibbs energy will be determined by the equation

$$\Delta G = (r\bar{G}_\text{R} + s\bar{G}_\text{S} + \ldots) - (b\bar{G}_\text{B} + c\bar{G}_\text{C} + \ldots)$$

When all the substances are in a standard state coinciding with that of the *pure* components, the change in the Gibbs energy (sometimes called the **normal** or **standard affinity**) will be

$$\Delta G^\circ = (rG^\circ_\text{R} + sG^\circ_\text{S} + \ldots) - (bG^\circ_\text{B} + cG^\circ_\text{C} + \ldots)$$

Hence

$$\Delta G - \Delta G^\circ = [r(\bar{G}_\text{R} - G^\circ_\text{R}) + s(\bar{G}_\text{S} - G^\circ_\text{S}) + \ldots] -$$
$$- [b(\bar{G}_\text{B} - G^\circ_\text{B}) + c(\bar{G}_\text{C} - G^\circ_\text{C}) + \ldots]$$

This equation holds for any system, both homogeneous and heterogeneous. The only requirement is the condition that the standard change in the Gibbs energy should correspond to such states of the reactants and products for which the activity of *each* of them will equal unity during the *entire* process.

If we are speaking, for instance, of the reaction

$$CO + 2H_2 = CH_3OH(g)$$

this condition means that during the entire process $p_{CO} = p_{H_2} = p_{CH_3OH} = 1$, i.e. the total pressure equals three atmospheres. The retaining of a constant pressure is possible provided that the reaction (the "vanishing" of 1 mole of CO and 2 moles of H_2 and the "appearance" of 1 mole of CH_3OH) does not result in a change in the properties of the mixture, i.e. that the initial amount of each component in comparison with the amount of the reacted and formed substances is very great (strictly speaking, *infinitely great*). The need to have a practically unchanged concentration of each of the reagents follows from the fact that only in this case will the partial molar Gibbs energies of each component remain constant during the process being considered.

Since the change in the Gibbs energy when one mole of the i-th substance transforms from the chosen standard state to a given one, by Eq. (6.35), is

$$\bar{G}_i - G_i^\circ = RT \ln \frac{f_i}{f_i^\circ} = RT \ln a_i$$

then

$$\Delta G - \Delta G^\circ = RT \ln \frac{a_R^r a_S^s \cdots}{a_B^b a_C^c \cdots} \tag{13.3}$$

But in equilibrium $\Delta G = 0$ [Eq. (5.31)], hence

$$-\Delta G^\circ = RT \ln \left[\frac{a_R^r a_S^s \cdots}{a_B^b a_C^c \cdots}\right]_{eq} \tag{13.4}$$

The quantities a_R, a_S, etc. in Eq. (13.4) are the *equilibrium* activities of the reagents in contrast to the quantities in Eq. (13.3), where they are the activities corresponding to *any* moment of the reaction, in particular to the initial state of the system.

In accordance with Eq. (13.4), Eq. (13.3) can be written down in the form

$$\Delta G = RT \ln \frac{a_R^r a_S^s \cdots}{a_B^b a_C^c \cdots} - RT \ln \left[\frac{a_R^r a_S^s \cdots}{a_B^b a_C^c \cdots}\right]_{eq} =$$

$$= RT \ln \frac{a_R^r a_S^s \cdots}{a_B^b a_C^c \cdots} - RT \ln K_a \tag{13.5}$$

where

$$K_a = \left[\frac{a_R^r a_S^s \cdots}{a_B^b a_C^c \cdots}\right]_{eq} \tag{13.6}$$

(in the following the subscript "eq" will be omitted).

The quantity K_a characterizing stable equilibrium of a system appearing as a result of a given reversible chemical reaction is the **thermodynamic equilibrium constant.** [Since activities are abstract quantities, the equilibrium constant is also dimensionless — a conclusion following directly both from Eq. (13.4) and from a comparison of the dimensions of ΔG° and RT.]

Equation (13.6) is a general expression of the law of mass action. For ideal systems (for which the activity of a component equals its concentration), it transforms into an equation of the law of mass action in whose form in the simplest case it can be found with the aid of kinetic notions. The derivation of Eq. (13.6) given above is general and not based on any notions of the mechanism of a process.

For a gas, we have $a_i = f_i$; therefore for reactions in the gaseous phase $K_a = K_f$, i.e. the equilibrium constant includes the fugacities of the components of an equilibrium gas mixture. If the pressure in a system is not great, then $f_i = p_i$ and $K_a = K_f = K_p$, i.e. the equilibrium constant is expressed through the equilibrium partial pressures:

$$K_p = \frac{p_R^r p_S^s \cdots}{p_B^b p_C^c \cdots}$$

The equilibrium constant can also be expressed through the equilibrium concentrations, i.e.

$$K_c = \frac{c_R^r c_S^s \cdots}{c_B^b c_C^c \cdots}$$

(c_i is in mol/dm^3). Hence in accordance with the fact that for a component of a mixture of ideal gases

$$p_i = \frac{n_i}{V} RT = c_i RT$$

we get

$$K_p = K_c(RT)^{\Delta n} \tag{13.7}$$

where Δn is the change in the number of moles of the gaseous reagents.

It follows from Eq. (13.7) that the relationship between K_p and K_c is determined by the sign of Δn and that $K_p = K_c$ only if $\Delta n = 0$,

because the case $RT = 1$ cannot have any practical importance (it corresponds to $T = 12.2$ K).

The equations determining the quantities K_p and K_c are absolutely accurate at $p \to 0$, because only at $p \to 0$ does Dalton's law, which these equations are based on, hold for any gases. For practical purposes, however, these equations can also be considered true at $p \approx 1$. In the general case, it should be understood that K_p and K_c are not true equilibrium constants: if $f_i \neq p_i$, then K_p (K_c), unlike K_f, will depend not only on temperature, but also on pressure, and on the ratio between the reagents as well. Thus, for the reaction

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$$

at 457 °C the value of K_p grows by about 35% when the pressure increases from 1 to 300 atm, i.e. it is not a true equilibrium constant.

Equation (13.4) in accordance with Eq. (13.6) can be written down in the form

$$\Delta G^\circ = -RT \ln K_a = -4.576T \log K_a \qquad (13.8)$$

Equations (13.5) and (13.8) are among the most important in chemical thermodynamics and are called equations of the **isotherm of a chemical reaction.**

Examination of Eqs. (13.3) and (13.5) shows that chemical affinity changes depending on the initial (arbitrary) concentrations of the reagents, pressure and temperature. But if $\Delta G = \varphi(p, T, n_B, n_C, \ldots, n_R, n_S, \ldots)$, then since the choice of the standard state already fixes the pressure and the aggregate state of the reagents, the quantity ΔG° depends only on temperature. In other words, for a reaction being considered at a given temperature, a *single* value of ΔG° corresponds to the *countless* values of ΔG. It follows that the numerical value of the equilibrium constant K_a depends only on the choice of the standard state for a given process at a given temperature.

If $(\partial K_a/\partial p)_T = 0$, then in the general case $\partial K_a/\partial p \neq 0$, because a change in pressure may be attended by a change in temperature, which leads to a change in the equilibrium constant.

13.4. INFLUENCE OF TEMPERATURE ON EQUILIBRIUM CONSTANT

Writing down Eq. (5.26) for a standard reaction, we get

$$\frac{d}{dT}\left(\frac{\Delta G^\circ}{T}\right) = -\frac{\Delta H^\circ}{T^2}$$

Using in it the value of ΔG° from Eq. (13.8), after transformations we get the **van't Hoff equation**

$$\frac{d \ln K_a}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{13.9}$$

where ΔH° is the standard heat effect of a reaction (not $\Delta \bar{H}^\circ$, because the *pure* state of all the reagents was taken as their standard state).

In the following (Chap. 15), the superscript ° will be used only to retain unity of generally adopted symbols. This reservation is explained by the insignificant dependence of ΔH on pressure (and concentration). Since K_a depends only on temperature, the substitution of the equation $(\partial \ln K_a/\partial T)_p = \Delta H/RT^2$ for Eq. (13.9) is superfluous. Therefore, Eq. (13.9) should be called an **equation of a reaction isobar** only in the sense that it includes the isobaric heat effect, whereas the equation

$$\left(\frac{\partial \ln K_p}{\partial T}\right)_p = \frac{\Delta H}{RT^2} \tag{13.10}$$

being a special case of the preceding one, is also an isobar relative to K_p, because $K_p = \varphi(p)$.

If the pure state of each reagent at $c_i = 1$ were selected as the standard state, then Eq. (13.10) would become

$$\frac{d \ln K_a}{dT} = \frac{\Delta U^\circ}{RT^2}$$

and, in particular, for an ideal solution

$$\frac{d \ln K_c}{dT} = \frac{\Delta U^\circ}{RT^2}$$

or in the general form

$$\left(\frac{\partial \ln K_c}{\partial T}\right)_V = \frac{\Delta U}{RT^2}$$

which is usually called the **equation of a reaction isochor.** Strictly speaking, this is precisely the equation that was derived by J. van't Hoff (1885), and it is related to the equation of an isobar, because both of them agree with Eqs. (13.7) and (6.10).

Equation (13.9) has great significance : the use of the equilibrium constant may be extended to any kind of equilibrium, including homogeneous and heterogeneous reactions and phase equilibria in one-component and multi-component systems. Therefore, for example, Eqs. (7.2) and (9.2) can be considered as particular cases of

Eq. (13.9), the former when $K_a = p$, and the latter when $K_a = x_2$. But this identity is formal: in Eq. (13.9) the quantity ΔH° is the heat effect of a retarded process (a standard reaction), whereas in Eq. (7.2) ΔH is the heat effect of an equilibrium transition. It must be noted, however, that the transition from standard to real conditions has virtually no influence on the value of the heat effect.

It follows from Eq. (13.9) that K_a grows with increasing temperature in processes attended by the absorption of heat ($\Delta H^\circ > 0$). If the standard reaction is exothermic, i.e. $\Delta H^\circ < 0$, then K_a grows with diminishing temperature. Thus, in accordance with the Le Chatelier principle, the nature of displacement of equilibrium under the influence of temperature is determined by the sign of the heat effect: upon heating, the reaction shifts in the direction of the absorption of heat, because this prevents a rise in the temperature in the system (see also Sec. 14.3).

Example 3. In the production of hydrogen by the iron and steam process, the following reactions proceed in the period of reduction:

$$Fe_3O_4 + H_2 = 3FeO + H_2O(g) \qquad (a)$$

and

$$FeO + H_2 = Fe + H_2O(g) \qquad (b)$$

Use the data of Table 1 to determine the influence of temperature on their direction.

Solution. From Table 1, using Hess's law, we get $\Delta H^\circ_{298} = 19\,300$ and 5600 cal/mol for reactions (a) and (b), respectively. The sign of ΔH° indicates that elevation of the temperature favours reduction. Since $\Delta H^\circ_1 > \Delta H^\circ_2$, then $(K_a)_1$ grows with increasing temperature at a faster rate than $(K_a)_2$.

13.4.1. Approximate Integration

If we assume in a first approximation that ΔH° is constant ($\Delta C_p = 0$), then it follows from Eq. (13.9) that

$$\left.\begin{aligned} \log K_a &= -\frac{\Delta H^\circ}{4.576T} + \text{const} \quad \text{or} \quad \log K_a = \frac{A}{T} + B \\ \Delta H^\circ &= -4.576 \frac{d \log K_a}{dT^{-1}} = -4.576 \log \alpha \end{aligned}\right\} \qquad (13.11)$$

whence

$$\log \frac{(K_a)_{T_2}}{(K_a)_{T_1}} = \frac{\Delta H^\circ}{4.576}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (13.12)$$

where A and B = constants

α = angle formed by the straight line $\log K = \varphi(T^{-1})$ and the axis of abscissas.

A graph of this kind is shown in Fig. 163. It gives exhaustive data only for one reaction; for the remaining ones it gives only the most reliable values calculated from rounded-off values of the temperature.

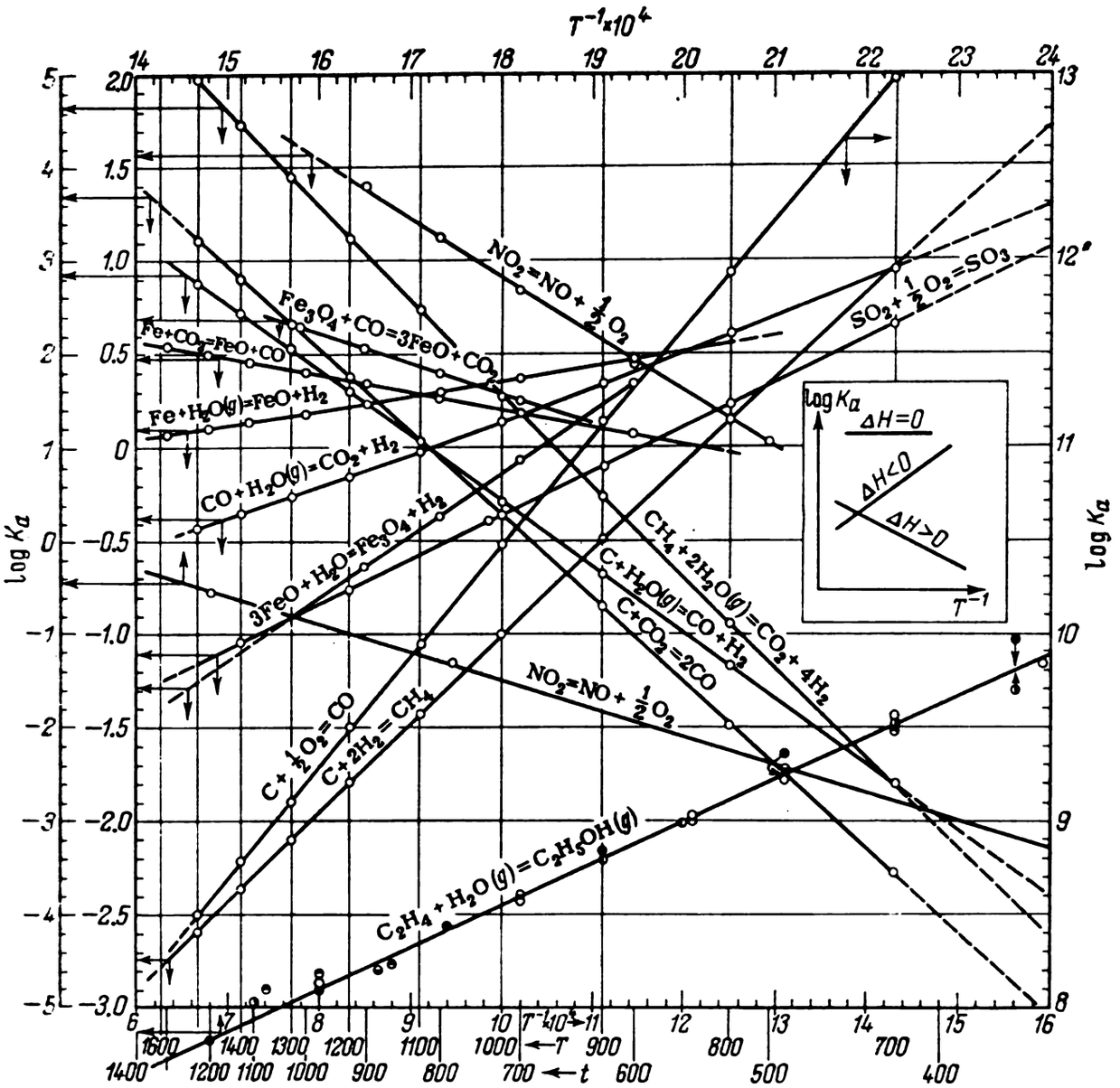


Fig. 163. Dependence of the logarithm of the equilibrium constant for selected reactions on the inverse absolute temperature. [Data obtained by different authors are given for the reaction $C_2H_4 + H_2O(g) = C_2H_5OH(g)$.]

Checking of Eq. (13.11)

A summary of the constants A and B for the reactions of formation of selected compounds from simple substances is given in Table 13.

If the heat effect and the equilibrium constant are known for the same temperature, then Eq. (13.11) and the corresponding

graph can be used to find the value of the equilibrium constant for any temperature. The values of $(K_a)_{T_1}$ and $(K_a)_{T_2}$ can be used to find the mean value of $\Delta H°$ for a given temperature interval.

Table 13. **Values of the Constants of Eq. (13.11) for Reactions of Formation of Selected Gaseous Compounds from Simple Substances**

Compound	A	B	Compound	A	B
CO	5 773	4.664	n-C_4H_{10}	6 589	−19.09
CO_2	20 550	0.148	n-C_5H_{12}	7 645	−24.25
HCl	4 821	0.634	n-C_6H_{14}	8 733	−29.23
H_2O	12 630	−2.320	n-C_8H_{18}	10 900	−39.42
NH_3	2 413	−5.168	CH_3OH	10 550	−8.60
CH_4	3 907	−3.767	C_2H_5OH	12 250	−11.65
C_2H_2	−11 800	3.073	CH_3OCH_3	9 613	−12.48
C_2H_4	−2 740	−2.781	$C_2H_5OC_2H_5$	13 170	−22.74
C_2H_6	4 425	−9.051	HCOH	−1 570	−0.74
C_3H_6 (propene)	−1 066	−7.627	CH_3COH	8 697	−5.82
C_3H_8	5 422	−14.07	CH_3Cl	4 502	−4.00
C_4H_8 (butene-1)	66	−12.51	C_2H_5Cl	5 616	−8.94

This method of calculating $\Delta H°$ is similar to the methods of determining the heats of vaporization and solution [compare Fig. 163 with Figs. 54 (p. 211) and 81 (p. 288)]. In the general case, the application of Eq. (13.12) to reactions proceeding at comparatively low temperatures gives the most accurate results.

If the standard Gibbs energies and heat effects are known, it is better to write down Eq. (13.12) in the form

$$\log (K_a)_T - \log (K_a)_{298} = \frac{\Delta H^\circ_{298}}{1364} - \frac{\Delta H^\circ_{298}}{4.576T}$$

or in accordance with Eq. (13.8)

$$\log (K_a)_T = 0.000\,733\,(\Delta H^\circ_{298} - \Delta G^\circ_{298}) - \frac{\Delta H^\circ_{298}}{4.576T} \qquad (13.13)$$

These equations are useful for assessing the possibility of a reaction for which only data at $t = 25\,°C$ are available. They are inaccurate, especially for elevated temperatures, because generally the value

$$\Delta H° \approx \frac{1}{2}(\Delta H^\circ_{T_1} + \Delta H^\circ_{T_2})$$

is used in calculations according to Eq. (13.12), while Eq. (13.13) contains the heat effect corresponding to one of the extreme temperatures. At a low heat effect and when it does not change uniformly with temperature, the mean arithmetic value of $\Delta H°$ will not satisfy the temperature dependence of K_a.

If $\Delta H°$ changes linearly within a given temperature interval, Eq. (13.12) may be used within a broader interval, but now ΔH will correspond to the temperature

$$T = T_1 T_2 \frac{\ln T_2/T_1}{T_2 - T_1} \tag{13.14}$$

Example 4. Use the data given below on the reaction of cracking of methane to determine the mean value of $\Delta H°$ within the temperature intervals 700-800, 1100-1200 and 1400-1500 K. Compare the results with those of graphical calculations.

T	700	800	900	1 000	1 100	1 200	1 300	1 400	1 500
$\Delta G°$	3 050	550	−2 010	−4 610	−7 220	−9 850	−12 500	−15 140	−17 800

Solution. We compute K_a by Eq. (13.8); from Eq. (13.12) we get $\Delta H_1° = 20\,550$, $\Delta H_2° = 21\,710$ and $\Delta H_3° = 22\,100$ cal/mol, respectively (the deviation from the most accurate values does not exceed 100 cal). After constructing a graph of $\log K_a$ against T^{-1} (see Fig. 163), we find the mean value of the heat effect of the reaction being considered for the interval from 700 to 1500 K from the angle of inclination of the straight line in accordance with Eq. (13.11):

$$\Delta H° = -4.576 \frac{-0.95 - 2.59}{(14.6 - 6.67)\ 10^{-4}} = 21\,240$$

Example 5. The values of $\Delta H°_{1100}$ for the reactions

$$CO + H_2O(g) = CO_2 + H_2 \tag{a}$$

and

$$CH_4 = C + 2H_2 \tag{b}$$

are −8070 and 21 650 cal/mol (see Fig. 16, p. 75), and of $\Delta G°_{1100}$ are 125 and 7220 cal/mol, respectively.

1. Use Eq. (13.11) to calculate $\log K_a = \varphi(T)$ for the interval from 700 to 1500 K (through every 200 kelvins) and compare the results with the data in Fig. 163.

2. Assess the possibility of calculation with the aid of tabulated values of ΔH°_{298} and ΔG°_{298}.

Solution. 1. Introducing into Eq. (13.11) the values of ΔH° and K_a found by Eq. (13.8), we get the values of the coefficient B in Eq. (13.11). They are —1.628 (a) and 5.737 (b). Therefore, for reaction (a) we have $\log K_a = 1764/T - 1.628$ and for reaction (b) we have $\log K_a = -4732/T + 5.737$.

2. After taking the values of ΔH°_{298} and ΔG°_{298} for the corresponding substances from Table 1 and Appendix 11, we get for reaction (a)

$$\Delta H^\circ_{298} = (\Delta H^\circ_{298})_{CO_2} - (\Delta H^\circ_{298})_{CO} - (\Delta H^\circ_{298})^g_{H_2O} = -9840 \text{ cal/mol}$$

and similarly $\Delta G^\circ_{298} = -6843$ cal/mol. For the second reaction $\Delta H^\circ_{298} = 17\,880$ and $\Delta G^\circ_{298} = 12\,146$ cal/mol. These data in accordance with Eq. (13.13) give the following results: for reaction (a) $\log K_a = 2151/T - 2.197$ and for reaction (b) $\log K_a = -3908/T + 4.205$.

The results of the calculations are given below. They are compared with the accurate values of $\log K_a$ (see Fig. 163)

T, K		700	900	1100	1300	1500
	$CO + H_2O(g) = CO_2 + H_2$					
$\log K_a$	accurate value	0.96	0.34	—0.02	—0.26	—0.43
	1	0.89	0.33	—0.02	—0.27	—0.45
	2	0.88	0.19	—0.24	—0.54	—0.76
	$CH_4 = C + 2H_2$					
$\log K_a$	accurate value	—0.95	0.49	1.43	2.10	2.59
	1	—1.02	0.48	1.43	2.10	2.58
	2	—1.38	0.14	0.65	1.20	1.60

The inaccuracy of calculations according to ΔH°_{298} and ΔG°_{298} is explained by the initial data being far beyond the limits of the given temperature interval. The first method gives good results notwithstanding the assumption that ΔH° is constant within a temperature interval of 800 kelvins. The greater accuracy of the calculations for the second process is explained by the comparatively insignificant change in ΔH° with temperature (see Fig. 16).

Example 6. For the reaction

$$CO + H_2O(g) = CO_2 + H_2$$

the equilibrium constants are $(K_a)_{500} = 126.0$ and $(K_a)_{1500} = 0.3704$. Calculate $\Delta H°$ and use this example to assess the reliability of Eq. (13.14) if within the indicated temperature interval the value of $\Delta H°$ changes linearly with the temperature (by about 235 cal per 100 kelvins).

Solution. From Eq. (13.12), we have $\Delta H° \approx 8690$ cal/mol. According to Eq. (13.14), $T = 824$ K corresponds to the found value of $\Delta H°$. The accurate value of $\Delta H°_{824}$ found with the aid of Hess's law (from Fig. 16) differs from the calculated value by 0.6%, whereas the mean arithmetic value ($\Delta H°_{1000} = 8310$ cal/mol, see Fig. 16) differs by 4.6%.

Some Regularities. The equation

$$\Delta G° = a + bT \qquad (13.15)$$

obtained by combining Eqs. (13.8) and (13.11) is often used for approximate calculations.

This simplification is quite justified in the absence of reliable experimental data, when we have to resort to analogies between a given substance and others having close properties in order to find the equation $K_a = \varphi(T)$.

The values of properties predicted on the basis of the known properties of a small number of compounds of the relevant class or homologous series are often used instead of the experimental determination of these properties. Data of this kind relating to $\Delta G°_{298}$ are given in Appendix 11.

It is easiest to establish a regularity for the simplest organic compounds, hydrocarbons; moreover, because the thermodynamics of hydrocarbons during the last decades has become especially important in connection with the broad application of a number of new organic reactions (cracking, pyrolysis, the synthesis of petrol, the conversion of olefins into higher alcohols, etc.).

Experimental data on the temperature dependence of $\Delta G°$ have been summarized in a number of empirical equations.

Thus, the following approximate equations have been proposed:

for *n*-alkanes

$$\Delta G° = -10\,550 - 5890n + 25.2nT - 2.2T \qquad (13.16)$$

for 1-alkenes (α-olefins)

$$\Delta G° = 20\,321 - 5835n + 24.52nT - 33.26T \qquad (13.17)$$

for alkynes

$$\Delta G° = 70\,425 - 8633n + 26.09nT - 67.5T \qquad (13.18)$$

and for the simplest polymethene hydrocarbons

$$\Delta G^\circ = 10\,375 - 8633n + 26.09nT - 15.19T \qquad (13.19)$$

where n is the number of carbon atoms in a compound.

The error in calculations by Eqs. (13.16)-(13.19) is up to approximately 500 cal/mol.

13.4.2. Accurate Integration

For accurate calculations and with big temperature intervals in integrating Eq. (13.9), account must be taken of the temperature dependence of the heat effect of a reaction.

Combining Eq. (13.9) with the equation $\Delta H^\circ = \Delta H_0^\circ + \Delta aT + \frac{1}{2}\Delta bT^2 + \frac{1}{3}\Delta cT^3 - \Delta c'/T$ [Eq. (3.29)] and integrating, we get

$$\ln K_a = -\frac{\Delta H_0^\circ}{RT} + \frac{1}{R}\int\frac{dT}{T^2}\int\Delta C_p\,dT + I' =$$

$$= -\frac{\Delta H_0^\circ}{RT} + \frac{\Delta a}{R}\ln T + \frac{\Delta b}{2R}T + \frac{\Delta c}{6R}T^2 + \frac{\Delta c'}{2R}T^{-2} + I'$$

or

$$\log K_a = -\frac{\Delta H_0^\circ}{4.576T} + \frac{\Delta a}{1.987}\log T + \frac{\Delta b}{9.150}T +$$

$$+\frac{\Delta c}{27.45}T^2 + \frac{\Delta c'}{9.150}T^{-2} + I'' \qquad (13.20)$$

or in accordance with Eq. (13.8)

$$\Delta G^\circ = \Delta H^\circ - T\int\frac{dT}{T^2}\int\Delta C_p\,dT + IT =$$

$$= \Delta H_0^\circ - \Delta aT\ln T - \frac{1}{2}\Delta bT^2 - \frac{1}{6}\Delta cT^3 - \frac{1}{2}\Delta c'T^{-1} + IT \qquad (13.21)$$

The integration constants of these equations are related by the obvious equation

$$I = -45.76I'' = -1.987I' \qquad (13.22)$$

Equation (13.21) can also be found by direct integration of Eq. (5.26) as applied to a standard reaction.

Equations (13.20) and (13.21) may be used for calculations only within the temperature interval for which the relationships for the heat capacities hold.

In the general case, to calculate ΔG° and thus to find the equilibrium constant for any temperature, we must know (1) the dependence of C_p on T (theoretically of C_p° on T) for all the reagents; (2) one value of ΔH; and (3) the value of K_a or ΔG° for at least one temperature.

The first two requirements are connected with the need to have the value of the integration constant ΔH_0° of Eq. (3.29) (see Sec. 3.5.2). The third is due to the fact that the integration constant of Eq. (13.20) or (13.21) must be known before we can calculate ΔG° or K_a for a given temperature.

Inserting $(K_a)_T$ into Eq. (13.20) or ΔG_T° into Eq. (13.21), we find the integration constant I'' or I. After this, it becomes possible to determine K_a or ΔG° for any temperature. The calculations will be simplified if we use tabulated values of ΔG_{298}° (Appendix 11) or special methods of calculation (see below).

Having at our disposal values of K_a or ΔG° for two temperatures and simultaneously solving Eqs. (3.29) and (13.21), we can find both integration constants, i.e. ΔH_0° and I.

When the relevant tabulated data are available, the calculations are also conducted using the reduced Gibbs energy

$$\frac{G_T^\circ - H_{T_1}^\circ}{T} = \frac{H_T^\circ - H_{T_1}^\circ}{T} - S_T^\circ$$

where the basic temperature T_1 equals either zero or 298 K. These functions are generally tabulated using 100-kelvin intervals. They are convenient, because unlike G_T° and ΔG_T° they change very slightly with a change in temperature, and this facilitates interpolation. The reduced Gibbs energies are determined for gases on the basis of spectral data (see Chap. 15), and for solids obeying the third law of thermodynamics by the equation

$$\frac{G_T^\circ - H_0^\circ}{T} = \frac{1}{T}\int_0^T \left(\int_0^T \frac{C_p}{T}\, dT\right) dT - \int_0^T \frac{\int_0^T C_p\, dT}{T}$$

or

$$\frac{G_T^\circ - H^\circ}{T} = \frac{1}{T}\int_0^T C_p dT - \int_0^T \frac{C_p\, dT}{T}$$

When the values of $(G_T^\circ - H_0^\circ)/T$ are available for all the reagents, the following equation can be used for calculations:

$$\Delta G_T^0 = \Delta H_{T_1}^\circ + T\Delta\left(\frac{G_T^\circ - H_0^\circ}{T}\right) - \Delta(H_{T_1}^\circ - H_0^\circ) \qquad (13.23)$$

If the standard heat effects are known for a temperature other than the basic one for which values of $(G_T^\circ - H_{T_1}^\circ)/T$ are available, the equations

$$\Delta G_T^\circ = \Delta H_{298}^\circ + T\Delta\left(\frac{G_T^\circ - H_0^\circ}{T}\right) + \Delta(H_{298}^\circ - H_0^\circ) \qquad (13.24)$$

and

$$\Delta G_T^\circ = \Delta H_{T_1}^\circ + T\Delta\left(\frac{G_T^\circ - H_{T_1}^\circ}{T}\right) \qquad (13.25)$$

should be used instead of Eq. (13.23).

Method of Sigma-Function. If we know a number of values of K_a for several temperatures, we can use a graphical procedure to simultaneously find ΔH_0° and I: rewriting Eq. (13.20) in the form

$$\Sigma = -4.576 \log K_a + 2.303\ \Delta a \log T + \frac{1}{2}\Delta bT +$$

$$+ \frac{1}{6}\Delta cT^2 + \frac{1}{2}\Delta c'T^{-2} = \frac{\Delta H_0^\circ}{T} + I \qquad (13.26)$$

we find that the left-hand side of Eq. (13.26) is a linear function of T^{-1}. The graph $\Sigma = \varphi(T^{-1})$ is a straight line whose slope equals ΔH_0° and whose ordinate intercept equals the integration constant I (Fig. 164).

The latter can be found in a different way: after inserting into the equation $\Sigma = \varphi(T)$ the value of ΔH_0° found from the graph, we calculate for each temperature the value of I and then determine its average value.

The above procedure is especially convenient when processing numerous experimental data in order to find an accurate equation $K_a = \varphi(T)$. It can also be used for determining $\Delta H^\circ = \varphi(T)$; this is expedient when we have authentic equilibrium constants and values of the heat capacity of the reagents, while the heat effects are unknown or doubtful.

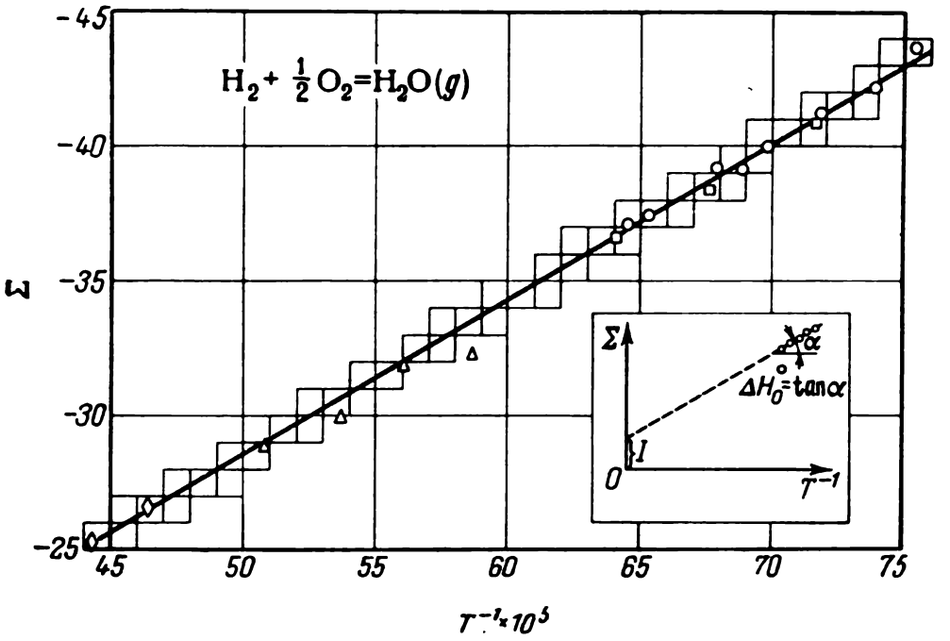


Fig. 164. Dependence of Σ-function on the inverse absolute temperature.
Checking of Eq. (13.26). (See Example 8)

Example 7. Find the equation $\Delta G^\circ = \varphi(T)$ for the reaction

$$CH_4 + H_2O(g) = CO + 3H_2$$

if $(K_a)_{1000} = 26.56$, $\Delta H^\circ_{298} = 49\,260$ cal/mol (according to Table 1 on the basis of Hess's law), and the temperature dependence of the heat capacity of the reagents is expressed by the equations

$$(C_p)_{CO} = 6.25 + 2.091 \times 10^{-3}T - 0.459 \times 10^{-6}T^2$$

$$(C_p)_{H_2} = 6.88 + 0.066 \times 10^{-3}T + 0.279 \times 10^{-6}T^2$$

$$(C_p)_{CH_4} = 3.422 + 17.845 \times 10^{-3}T - 4.165 \times 10^{-6}T^2$$

$$(C_p)^g_{H_2O} = 7.219 + 2.374 \times 10^{-3}T + 0.267 \times 10^{-6}T^2$$

Solution.

$$\Delta C_p = [(C_p)_{CO} + 3(C_p)_{H_2}] - [(C_p)_{CH_4} + (C_p)^g_{H_2O}] =$$

$$= 16.249 - 17.930 \times 10^{-3}T + 4.276 \times 10^{-6}T^2$$

Introducing in Eq. (3.29) the values of $\Delta H^\circ_{298} = 49\,260$, $\Delta a = 16.249$, $\Delta b = -17.930 \times 10^{-3}$ and $\Delta c = 4.276 \times 10^{-6}$, we find $\Delta H^\circ_0 = 45\,174$ cal/mol. Hence the equation $\Delta G^\circ = \varphi(T)$ will be written down in the form

$$\Delta G^\circ = 45\,174 - 16.249T \ln T + 8.965 \times 10^{-3}T^2 - 0.712 \times 10^{-6}T^3 + IT$$

Inserting in this equation the value of $\Delta G^\circ_{1000} = -6517$ calculated according to the value of K_a by Eq. (13.8), we find the integration constant $I = 52.318$. Therefore, for the process of conversion of methane with steam we have

$$\Delta G^\circ = 45\,174 - 37.42T \log T + 8.965 \times 10^{-3}T^2 - \\ - 0.712 \times 10^{-6}T^3 + 52.318T$$

Hence in accordance with Eq. (13.8), Eq. (13.20) will become

$$\log K_a = -\frac{9872.8}{T} + 8.1794 \log T - 1.9596 \times \\ \times 10^{-3}T + 0.1556 \times 10^{-6}T^2 - 11.433$$

The results of calculating ΔG° according to the found equation are compared below with the most authentic data:

T	300	700	1100	1500
ΔG°, calculated	33 868	11 436	−12 577	−36 869
ΔG°, accurate	33 873	11 437	−12 563	−36 869

Example 8. Studying the equilibrium of the reaction

$$H_2 + \frac{1}{2}O_2 = H_2O(g)$$

gave the following results:

T	1325	1354	1393	1397	1433	1455	1474	1480	1531
$K_a \times 10^{-5}$	76.5	41.3	24.7	20.5	13.5	8.35	8.45	5.66	3.47
T	1550	1561	1705	1783	1863	1968	2155	2257	
$K_a \times 10^{-5}$	29.1	22.6	2.3	1.82	6.70	3.79	10.94	5.90	

Using the sigma-function method, find the equation $\Delta G^\circ = \varphi(T)$ for the above process. Assume that

$$(C_p)^g_{H_2O} = 8.22 + 0.15 \times 10^{-3}T + 1.34 \times 10^{-6}T^2$$

$$(C_p)_{H_2} = 6.62 + 0.81 \times 10^{-3}T$$

$$(C_p)_{O_2} = 6.26 + 2.746 \times 10^{-3}T - 0.770 \times 10^{-6}T^2$$

Solution. Since

$$\Delta C_p = -1.53 - 2.033 \times 10^{-3}T + 1.725 \times 10^{-6}T^2$$

Eq. (13.26) acquires the form

$$\Sigma = -4.576 \log K_a - 3.524 \log T - 1.0165 \times 10^{-3}T + \\ + 0.2875 \times 10^{-6}T^2 = \Delta H_0^\circ T^{-1} + I$$

After calculating the values of Σ for the temperatures indicated in the initial conditions, we plot a graph of $\Sigma = \varphi(T^{-1})$ (see Fig. 164, where the results obtained in various investigations are indicated). We draw a straight line through the points found in this way whose slope in accordance with Eq. (13.26) gives $\Delta H_0^\circ \approx -57\,500$, and the ordinate intercept, the constant $I = -0.10$ (to find the latter quantity, the axis of abscissas should be continued to the value $T^{-1} = 0$, as shown in the drawing in the bottom right-hand corner of the graph in Fig. 164). As a result, we get

$$\Delta G^\circ = -57\,500 + 3.524T \log T + 1.0165 \times 10^{-3}T^2 - \\ - 0.2875 \times 10^{-6}T^3 - 0.10T$$

For checking, we use the values of $\Delta C_p = \varphi(T)$ and $\Delta H_{298}^\circ = -57\,796$ cal/mol (see Table 1) to determine by Eq. (3.29) the value of $\Delta H_0^\circ = -57\,265$ cal/mol. It coincides with the adopted value of this constant within the limits of the errors of the initial data. If we use the most authentic values of $\Delta G_{298}^\circ = -54\,638$ cal/mol (see Table 14) and $\Delta H_0^\circ = -57\,265$ cal/mol to find the integration constant I by Eq. (13.26), it will equal -0.174. Although this value differs considerably from that found from the graph of $\Sigma = \varphi(T^{-1})$, it is small, and the discrepancy, equal in the general case to $0.074T$, is only 220 cal even at $T = 3000$ K. Therefore in approximate calculations, the last term of the found equation $\Delta G^\circ = \varphi(T)$ may in general be ignored.

Some Regularities. The calculation of $\Delta G^\circ = \varphi(T)$ can be based on the assumption that the standard Gibbs energy of formation is due to the nature and number of atomic bonds in a molecule of a compound, i.e. a definite value of the Gibbs energy of formation can be assigned to each type of bond. The value of ΔG° for a given substance can be determined by summation of these values (this method is similar to that described in Sec. 3.3.1 for calculating ΔH).

The values of ΔG° for various bonds can be found from the most accurate equations of $\Delta G^\circ = \varphi(T)$ for the corresponding substances. For instance, division of the equation $\Delta G^\circ = \varphi(T)$ for methane by four gives the relevant equation for a C—H bond. If we now subtract $18\Delta G_{C-H}^\circ$ from the equation $\Delta G^\circ = \varphi(T)$ for octane and divide the result by seven, we get ΔG_{C-C}°. Approximate equations for ΔG° of other bonds can be found in a similar way (V. Falkovsky, 1948).

Some of these equations are given below:

$$\left.\begin{aligned}
\Delta G^\circ_{C-H} &= -3344.5+2.97T\ln T-2.25\times10^{-3}T^2+0.188\times\\
&\quad\times10^{-6}T^3-13.68T\\
\Delta G^\circ_{C-C} &= 4437+0.421T\ln T+1.7\times10^{-3}T^2-0.62\times\\
&\quad\times10^{-6}T^3+9.53T\\
\Delta G^\circ_{C=C} &= 28\,024+2.75T\ln T-1.4\times10^{-3}T^2-0.80\times\\
&\quad\times10^{-6}T^3-24.86T\\
\Delta G^\circ_{C-CH_3} &= -7624+10.42T\ln T-5.7\times10^{-3}T^2-0.15\times\\
&\quad\times10^{-6}T^3-36.12T\\
\Delta G^\circ_{C-OH} &= -34\,984+5.18T\ln T-3.3\times10^{-3}T^2-0.311\times\\
&\quad\times10^{-6}T^3-18.6T\\
\Delta G^\circ_{C-C\diagup\!\!\!=\atop\quad\diagdown H} &= 22\,933-12.91T\ln T+6.84\times10^{-3}T^2-\\
&\quad-0.56\times10^{-6}T^3+50.13T\\
\Delta G^\circ_{C-COOH} &= -89\,867+6.29T\ln T-6.8\times10^{-3}T^2-0.56\times\\
&\quad\times10^{-6}T^3-7.37T
\end{aligned}\right\}\quad(13.27)$$

Simplified equations for some of the bonds can be written down as follows:

$$\left.\begin{aligned}
\Delta G^\circ_{C-H} &= -3845+3.0T\ln T-2\times10^{-3}T^2-13.7T\\
\Delta G^\circ_{C-C} &= 4440+0.4T\ln T+2\times10^{-3}T^2+9.5T\\
\Delta G^\circ_{C=C} &= 28\,020+2.8T\ln T-1\times10^{-3}T^2-24.9T\\
\Delta G^\circ_{C-CH_3} &= -7620+10.4T\ln T-6\times10^{-3}T^2-36.1T
\end{aligned}\right\}\quad(13.28)$$

The value of ΔG_T for the formation of organic compounds can be assessed on the basis of the change in this quantity due to a change in the structure of a molecule, in particular according to the method proposed by D. van Krevelen and H. Chermin, who recommended group components of the coefficients of Eq. (13.15). The latter are given in Appendix 11. They are approximate and in the majority of cases can serve only for orientation. More reliable data can be obtained by Eq. (5.22) on the basis of approximate values of ΔH°_{298} and ΔS°_{298} found by the methods treated in Sec. 3.3.1 and on p. 497, respectively.

Example 9. Find ΔG°_{1000} for the formation of C_4H_{10} from simple substances by Eqs. (13.16), (13.27) and (13.28).

Solution. By Eq. (13.16) we have $\Delta G^\circ_{1000} = -10\,550 - 5890 \times \times 4 + 25.2 \times 4 \times 1000 - 2.2 \times 1000 = 64\,490$ cal/mol.

By Eq. (13.27) we have $\Delta G^\circ = 10\Delta G^\circ_{C-H} + 3\Delta G^\circ_{C-C} = -20\,134 + + 30.963T \ln T - 17.4 \times 10^{-3}T^2 + 0.02 \times 10^{-6}T^2 - 108.21T$, whence $\Delta G^\circ_{1000} = 68\,200$ cal/mol.

By Eq. (13.28) we have $\Delta G^\circ = -25\,130 + 31.2T \ln T - 14 \times \times 10^{-3}T^2 - 108.5T$, whence $\Delta G^\circ_{1000} = 67\,930$ cal/mol. Accurate calculations give $\Delta G^\circ_{1000} = 64\,500$ cal/mol.

13.5. INDIRECT CALCULATION OF EQUILIBRIUM

13.5.1. Standard Gibbs Energies

The change in the Gibbs energy can be recalculated for any temperatures and pressures; therefore it is sufficient to know values of ΔG related to the same pressure and temperature. Generally the values of ΔG°_{298} are used. Such systematization of the material eliminates the possibility of errors that could creep in if the values of ΔG were related to different, although sufficiently close states of substances.

The quantities ΔG°_{298} (Table 14 and Appendix 2) are the change in the Gibbs energy which would be observed in an isothermal

Table 14. **Standard Gibbs Energies (in kcal/mol) of Formation of Selected Substances (See Also Appendix 2)**

Substance	ΔG°_{298}	Substance	ΔG°_{298}
CO(g)	−32.778	NO(g)	20.693
CO_2(g)	−94.259	NO_2^-(aq)	−8.86
$CaCO_3$(c)	−269.78	SO_2(g)	−71.752
H(g)	48.582	CH_4(g)	−12.146
HBr(g)	−12.75	C_2H_2(g)	49.827
HBr(aq)	−24.88	C_2H_4(g)	16.334
HCl(g)	−22.78	C_2H_6(g)	−7.883
HNO_3(aq)	−20.67	C_6H_6(lq)	29.72
H_2O(g)	−54.638	CH_3OH(lq)	−39.94
H_2O(lq)	−56.703	CH_3COOH(lq)	−93.06
H_2S(g)	−8.081	C_2H_5OH(lq)	−41.64
NH_3(g)	−3.993	C_6H_5Cl(lq)	21.32
NH_3(aq)	−6.37	$C_6H_5NO_2$(lq)	34.95
NH_4^+(aq)	−19.00	$C_6H_5NH_2$(lq)	35.63

process provided that the reacting simple substances and the compounds produced are each under a pressure of 1 atm (more precisely, have activities equal to unity), the former being in modifications that are stable at $t = 25\,°C$ and $p = 1$ atm. If the reagents are in a mixture or a solution, it is also necessary to indicate the standard concentration (for solutes $x_i = 1$); see p. 50.

Should a real gas in standard conditions deviate considerably from the ideal state, it is necessary to introduce a correction according to Eq. (5.25). *

The value of ΔG°_{298} for ions (see Appendix 2) is related to the value of this quantity for a hydrogen ion, taken equal to zero. The state of ions in a hypothetical ideal aqueous solution of molar concentration is taken as their standard state. The above unification is important not only because ΔG°_{298} (or in the general case ΔG°_T)** is related directly to the constant of chemical equilibrium, but also for another reason: the difference between the values of ΔG°_{298} (or ΔG°_T) of formation of two substances, like the difference between the values of ΔH°_{298} (or ΔH°_T), reflects only the difference in the nature of these substances.

It must be remembered that the temperature at which the vast majority of chemical processes occur is much higher than 25 °C, and therefore care should be taken when extrapolating the results of calculations for high temperatures. The reactions of synthesis of many substances in standard conditions are hypothetical. This cannot be an obstacle to the calculation of ΔG°_{298}, however, because the change in the Gibbs energy does not depend on the path of transition. At the same time if the tables contained values of ΔG°_{298} only for substances that are stable in standard conditions, then for very many reactions account would have to be taken in the calculations of corrections not only for the temperature and pressure differing from the standard ones, but also of the transition to other phases. The latter is not convenient, and it is therefore preferred to give data for unstable phases in the tables beforehand. We shall use an example to explain this.

The quantity ΔG°_{298} is used for $H_2O(g)$ in all calculations, although the state of water vapour in the form of an idealized gas at $p = 1$ atm and $t = 25\,°C$ cannot be achieved experimentally. Indeed, water vapour at 25 °C having even a considerably lower pressure than 1 atm spontaneously condenses, because the saturated vapour pressure at this temperature is only 0.031 26 atm. But the thermody-

* Corrections to ΔH may not be introduced for non-ideal conditions (when passing to the standard state), because in accordance with Eq. (4.23) the enthalpy will change with an increase in pressure only at very high pressures.

** The values of both quantities are given in reference books.

namic properties of vapour in these conditions can be found experimentally. The calculations are performed by the equation

$$(\Delta G^{g}_{298})^\circ = (\Delta G^{lq}_{298})^\circ + 1364 \log \frac{1}{p_{298}} \qquad (13.29)$$

where p_{298} is the saturated vapour pressure of a given substance at $t = 25\,^\circ C$ ($T = 298.2$ K).

Example 10. Use the data given in Table 14 to calculate ΔG°_{298} for the reaction

$$CO + 2H_2 = CH_3OH(g)$$

($p_{298} = 0.15$ for methanol).

Solution. From Table 14 for the reaction $CO + 2H_2 = CH_3OH(lq)$ we have $\Delta G^\circ_{298} = -39\,940 - (-32\,778) = -7162$, whence by Eq. (13.29) for the process $CH_3OH(lq) = CH_3OH(g)$ we get $\Delta G^\circ_{298} = -4.576 \times 298.2 \times \log 0.15 = 1120$ cal/mol. Therefore, for the synthesis of gaseous methanol $\Delta G^\circ_{298} = -7162 + 1120 = -6042$ cal/mol.

13.5.2. Calculation of Equilibrium Constant

The quantity ΔG°_{298} can be calculated for a given process according to a rule similar to that used in calculating the heat effects (see Sec. 3.1). This is still another method of calculating the equilibrium constant (in combining the data all the substances in all the reactions must be at identical pressure and temperature and in the same states of aggregation).

For the reaction

$$bB + cC + \ldots = rR + sS + \ldots$$

$$\Delta G^\circ_T = [r(\Delta G^\circ_R)_T + s(\Delta G^\circ_S)_T + \ldots] - [b(\Delta G^\circ_B)_T + c(\Delta G^\circ_C)_T + \ldots]$$

or according to Eq. (13.8)

$$(K_a)_T = \frac{(K_a)^r_R (K_a)^s_S \ldots}{(K_a)^b_B (K_a)^c_C \ldots}$$

where ΔG°_i and $(K_a)_i$ correspond to the reactions of formation of the relevant compounds from simple substances.

Such calculations can be performed for any temperature T if we have the values of ΔG°_T (or K_T) for all the reagents, and also for a certain temperature interval by combining the equations $\Delta G^\circ = \varphi(T)$ [or $K_a = \varphi(T)$] for the corresponding processes.

The indirect method of calculations permits us to reach exhaustive conclusions with respect to many reactions without resorting

to experiments, i.e. with the minimum expenditure of time. This method is of great importance in calculating complex equilibria, when several reactions proceed simultaneously (Sec. 14.4), and is especially helpful when it is difficult or impossible to study the equilibrium of a given reaction. In addition, with a high accuracy of the values used for the calculations, the indirect method permits us to check the validity of various data and thus assess the authenticity of different methods of studying equilibrium.

Example 11. The equations

$$\log (K_a)_a = \frac{6366}{T} 2.961 \log T + 0.7668 \times 10^{-3} T - 0.1764 \times$$

$$\times 10^{-6} T^2 + 2.3$$

$$\log (K_a)_b = -\frac{2413}{T} - 5.589 \log T + 1.025 \times 10^{-3} T + 0.175 \times$$

$$\times 10^{-6} T^2 + 13.0$$

were proposed for the reactions

$$C_2H_4 + H_2 = C_2H_6 \qquad (a)$$

$$2C + 2H_2 = C_2H_4 \qquad (b)$$

respectively. Find Eqs. (13.20) and (13.21) for the reaction

$$2C + 3H_2 = C_2H_6 \qquad (c)$$

Solution. Since reaction (c) is the sum of reactions (a) and (b), then $(K_a)_c = (K_a)_a (K_a)_b$ and $\log (K_a)_c = \log (K_a)_a + \log (K_a)_b$, i.e

$$\log (K_a)_c = \frac{3953}{T} - 8.55 \log T + 1.7918 \times 10^{-3} T -$$

$$- 0.14 \times 10^{-8} T^2 + 15.3$$

whence

$$\Delta G_c^\circ = -18\,085 + 39.116 T \log T - 8.198 \times 10^{-3} T^2 +$$

$$+ 0.8064 \times 10^{-5} T^3 - 70.0 T$$

13.6. CHEMICAL EQUILIBRIUM AND THE HEAT LAW

13.6.1. Reactions in Condensed Systems

The equations obtained earlier allow us to calculate the equilibrium constant for any temperature, but provided that it be determined without fail for at least one temperature : the value of the constant I in Eq. (13.21) cannot be computed beforehand, because the properties of the reagents affecting its value are not known. Being

independent of the temperature, it differs for different reactions. In other words, the indeterminacy of I hinders the determination of ΔG by integrating Eq. (5.26). It cannot be determined with the aid of the first and second laws of thermodynamics, which give only a differential relationship for chemical affinity (the investigation of a reaction in a galvanic cell is possible only for a few processes). Consequently, the problem of calculating equilibrium in a general form cannot be solved on the basis of the first and second laws of thermodynamics. This also follows from the fact that the equality $\Delta G = \Delta H$ is observed only in two special cases (see Sec. 13.1).

An attempt to determine I with the aid of the initial conditions does not give positive results: Eq. (5.26) written down in the form

$$\Delta G = -T\int \frac{\Delta H}{T^2} dT + IT$$

at $T = 0$ gives indeterminacy, which it is impossible to eliminate without additional assumptions. Thus, it is impossible to calculate ΔG_T according to the values of ΔG_0.

All this is illustrated by Fig. 165. The path of the curve $\Delta H = \varphi(T)$ is clear from thermal data, but the presence of I makes the position of the curve $\Delta G = \varphi(T)$ indefinite. The constant cannot be chosen arbitrarily, but must have a quite definite value, otherwise ΔG in general cannot be an unambiguous function of temperature. Without experimental data, we cannot choose a single curve of ΔG from among the infinitely great number of them differing in the value of I. If the value of the equilibrium constant is known for any temperature, this permits us to find the true curve. Indeed, knowing $(K_a)_T$ and thus ΔG_T, we can find the direction of the curve $\Delta G = \varphi(T)$ for a given value of I, since according to Eq. (5.26) it is only necessary to transfer the difference $\Delta H - \Delta G$ upward from the origin of coordinates (Fig. 166). Line *ab* gives the direction o

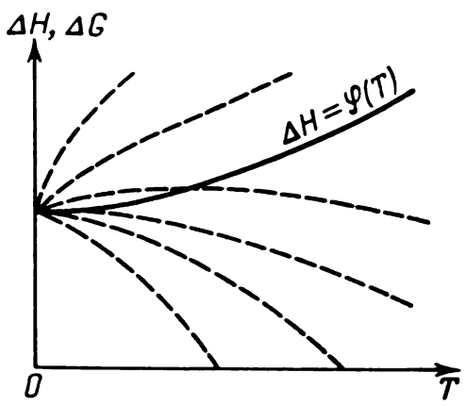


Fig. 165. Curves $\Delta H = \varphi(T)$ and $\Delta G = \varphi(T)$ for the low-temperature region

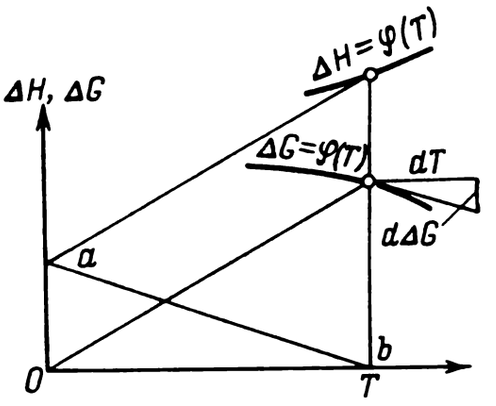


Fig. 166. Construction of curve $\Delta G = \varphi(T)$ according to curve $\Delta H = \varphi(T)$

a tangent to the curve of ΔG for ΔG_T, because $\partial(\Delta G)/\partial T = aO : Ob$. Constructing tangents to the curve by consecutive movement, we can draw the complete curve $\Delta G = \varphi(T)$.

Heat Law. W. Nernst (1906) advanced the assumption that the curves $\Delta H = \varphi(T)$ and $\Delta G = \varphi(T)$ have a common tangent at $T = 0$, i.e.

$$\lim_{T\to 0}\left[\frac{\partial(\Delta H)}{\partial T}\right]_p = \lim_{T\to 0}\left[\frac{\partial(\Delta G)}{\partial T}\right]_p \tag{13.30}$$

The subscripts p (and the superscript °) may be discarded, because for practical purposes ΔH and ΔG do not depend on the pressure in condensed systems. Therefore, the fact that the values of $\partial(\Delta H)/\partial T$ and $\partial(\Delta G)/\partial T$ belong to the region of temperatures close to $T = 0$ may be considered as their only limitation.

It follows from Eq. (5.26) that the derivative $\partial(\Delta G)/\partial T$ at $T = 0$ transforms into indeterminacy, because

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_{T\to 0} = \frac{(\Delta G)_{T\to 0} - (\Delta H)_{T\to 0}}{0} = \frac{0}{0}$$

But taking the ratio of the limits of the derivatives of the numerator and denominator of Eq. (5.26) to eliminate indeterminacy, we find by Eq. (13.30) that

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_{T\to 0} = \frac{[\partial(\Delta G)/\partial T]_{T\to 0} - [\partial(\Delta H)/\partial T]_{T\to 0}}{(\partial T/\partial T)_{T\to 0}} = 0$$

Hence, Eq. (13.30) can finally be written in the form

$$\lim_{T\to 0}\frac{\partial(\Delta H)}{\partial T} = \lim_{T\to 0}\frac{\partial(\Delta G)}{\partial T} = 0 \tag{13.31}$$

or in accordance with Eqs. (3.26) and (5.24)

$$\lim_{T\to 0}\Delta C_p = \lim_{T\to 0}\Delta S = 0 \tag{13.32}$$

Equations (13.31) and (13.32) are the initial form of the so-called **heat law (Nernst's theorem)** which relates only to condensed systems.

The heat law can be considered as the extension of Berthelot's principle from $T = 0$ to $T > 0$. This law was first proposed in the form of a hypothesis, but it was soon confirmed experimentally. It was found that in reactions proceeding between pure solid and liquid substances the difference between ΔH and ΔG is not great, and its change with a change in temperature in the region of low temperatures is insignificant.

It follows from Eq. (13.32) that the heat capacity of a condensed system at $T \to 0$ should not change during a reaction. Therefore the rule of additivity of heat capacities (see p. 71) is accurate only at and near absolute zero. (Similar conclusions could be derived for the isochoric heat capacity.)

Equation (13.32) also shows that *a process in condensed systems occurs without a change in entropy at absolute zero and near it.* For this reason, an adiabat and an isotherm coincide at $T = 0$.

The idea of the new law was originally expressed by the equation $(\Delta G)_{T\to 0} = (\Delta H)_{T\to 0}$ and Eq. (13.30).

It was later shown that its essence can be reduced to the condition

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_{T\to 0} = 0$$

Notwithstanding Eq. (13.31), it would seem that the equation $[\partial(\Delta H)/\partial T]_{T\to 0} = 0$ could also hold when $[\partial(\Delta G)/\partial T]_{T\to 0} \neq 0$. Indeed, on one hand

$$\lim_{T\to 0} \frac{\Delta G - \Delta H}{T} = \frac{[\partial(\Delta G)/\partial T]_{T\to 0} - [\partial(\Delta H)/\partial T]_{T\to 0}}{(\partial T/\partial T)_{T\to 0}} =$$

$$= \left[\frac{\partial(\Delta G)}{\partial T}\right]_{T\to 0} - \left[\frac{\partial(\Delta H)}{\partial T}\right]_{T\to 0}$$

and on the other

$$\lim_{T\to 0} \frac{\Delta G - \Delta H}{T} = \left[\frac{\partial(\Delta G)}{\partial T}\right]_{T\to 0}$$

whence

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_{T\to 0} = \left[\frac{\partial(\Delta G)}{\partial T}\right]_{T\to 0} - \left[\frac{\partial(\Delta H)}{\partial T}\right]_{T\to 0}$$

But it follows from the last relationship that $[\partial(\Delta H)/\partial T]_{T\to 0} = 0$ when the single requirement is observed that $[\partial(\Delta G)/\partial T]_{T\to 0} \neq 0$. This equation would also be observed if the heat law were not true and $[\partial(\Delta G)/\partial T]_{T\to 0} \neq 0$. Only when the heat law is observed are both derivatives equal.

Equation (13.31) shows that the curve $\Delta G = \varphi(T)$ should horizontally reach the axis of ordinates. Therefore, the curves $\Delta H = \varphi(T)$ and $\Delta G = \varphi(T)$ do not simply join each other at the point corresponding to absolute zero, but contact each other on the approach to this point. According to Eq. (13.31), they have a common horizontal tangent (Fig. 167*a*).

Thermodynamics cannot indicate how long the curves of ΔH and ΔG follow the same course, i.e. to what temperature the "principle of maximum work" holds and the additivity of heat capacities and entropies is observed. All that can be said is that the smaller the value of $\partial(\Delta G)/\partial T$, and hence that of $\Delta G - \Delta H$, the higher is

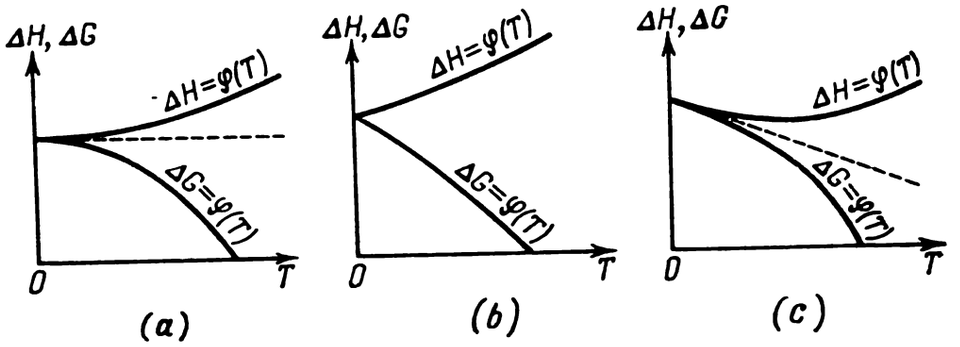


Fig. 167. Curves $\Delta H=\varphi(T)$ and $\Delta G=\varphi(T)$ [variant (a) is correct]

the temperature at which a process begins to emerge from the region of equality of the quantities ΔH and ΔG. For chemical (and electrochemical) processes in condensed systems, the curves of ΔH and ΔG begin to diverge appreciably at comparatively low temperatures (see, for example, Fig. 168). Conversely, $\Delta G = \Delta H$ at practically all temperatures for processes that take place only at the expense of the kinetic energy of motion (for instance purely mechanical processes) or at the expense of intranuclear energy (radioactive processes). In other words, the principle of maximum work holds for such processes at any temperatures.

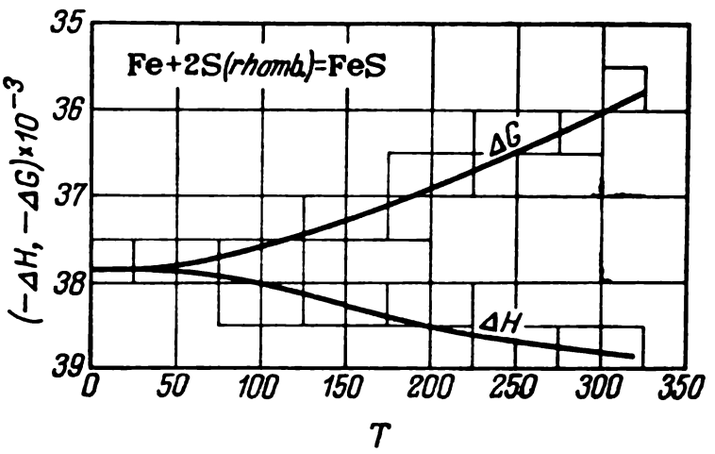


Fig. 168. Graphical calculation of $\Delta G = \varphi(T)$. (See Example 13)

13.6.2. Equations $\Delta H = \varphi(T)$ and $\Delta G = \varphi(T)$ for Condensed Systems

The heat law permits us to select a curve of ΔG for condensed systems on the basis of a curve of ΔH. The conclusions following from it may be extended to the region of high temperatures, but only provided that no phase transitions occur. Indeed, if, for example, one of the reagents at a certain temperature begins to sublime, a break will occur on the curve of ΔG at this point (since the value

of ΔS changes), while the curve of ΔH will move vertically (by ΔH_{subl}) and an inflection will appear on it (since the value of ΔG_p changes). The course of the curves of ΔH and ΔG will become absolutely different, and their extrapolation to $T = 0$ will not lead to the situation corresponding to Eq. (13.31) and Fig. 167*a*.

Therefore, the equations $\Delta H = \varphi(T)$ and $\Delta G = \varphi(T)$ for condensed systems, unlike the ones used previously, should be compiled on the basis of relationships for the heat capacities that hold down to absolute zero. These relationships differ from the usual ones, because the nature of the curve $C_p = \varphi(T)$ changes in the region of low temperatures (see Sec. 3.4.2). Bearing this in mind, we shall add the superscript "cd" to all the constants in the equations expressing the temperature dependence of the heat effect and the change in the Gibbs energy for condensed systems. The quantity ΔH_0^{cd}, unlike ΔH_0, has the physical meaning of the heat effect of a reaction at $T = 0$. In the same way, the constant I^{cd}, which remains unchanged down to absolute zero, acquires the meaning of the change in entropy at $T = 0$, i.e. it differs from the integration constant in Eq. (13.21).

Taking the derivatives $\partial(\Delta H^{cd})/\partial T$ and $\partial(\Delta G^{cd})/\partial T$ in accordance with Eq. (13.31), we get *

$$\Delta a^{cd} = 0 \tag{13.33}$$

$$I^{cd} = 0 \tag{13.34}$$

Therefore Eqs. (3.29) and (13.21)** for condensed systems should be written down in the form

$$\Delta H^{cd} = \Delta H_0^{cd} + \frac{1}{2}\Delta b^{cd}T^2 + \frac{1}{3}\Delta c^{cd}T^3 \tag{13.35}$$

$$\Delta G^{cd} = \Delta H_0^{cd} - \frac{1}{2}\Delta b^{cd}T^2 - \frac{1}{6}\Delta c^{cd}T^3 \tag{13.36}$$

---

* From the equation

$$\frac{\partial(\Delta G^{cd})}{\partial T} = -\Delta a^{cd}(1 + \ln T) - \Delta b^{cd}T - \frac{1}{2}\Delta c^{cd}T^2 + I^{cd}$$

it follows that Δa^{cd} can be either 0 or ∞. Indeed, if $\Delta a^{cd} \neq 0$, then at $T \to 0$ we have $\ln T \to -\infty$ and

$$\lim_{T\to 0} \frac{\partial(\Delta G^{cd})}{\partial T} = -\Delta a^{cd}(1 + \ln T) + I^{cd} = +\infty$$

which gives $\Delta a^{cd} = \infty$. But since this value of Δa^{cd} is absurd ($C_p = \infty$ corresponds to it), then $\Delta a^{cd} = 0$, and therefore $I^{cd} = 0$. Thus it is important that Δa^{cd} is not simply a very small quantity, but is zero.

** The first equation without the last, and the second without the next to last term, i.e. obtained on the basis of Eq. (3.22), because the use of Eq. (3.23) would give an absurd result: $\lim_{T\to 0} C_p$, ΔH, $\Delta G = \infty$.

In the following, the superscript "cd" will be discarded, but it should be remembered that it must be used whenever we are dealing with the properties of substances near absolute zero.

Inspection of Eqs. (13.35) and (13.36) shows that the curves of ΔH and ΔG diverge, while when $\Delta c = 0$, they are symmetrical. This does not mean that for any temperature the derivatives $\partial(\Delta H)/\partial T$ and $\partial(\Delta G)/\partial T$ will have different signs, because maxima and minima may appear on the curves of ΔH and ΔG for elevated temperatures. As indicated above, the found equations may be applied to elevated temperatures only for systems consisting of substances that do not change their state of aggregation when cooled to temperatures very close to absolute zero.

Equation (13.36) eliminates indeterminacy of the curve $\Delta G = \varphi(T)$, and therefore the graphical method of calculations can be used. The latter gives an accurate solution that does not depend on chance in selecting the functions for the heat capacities.

To construct a graph, we must know $\Delta C_p = \varphi(T)$ for the entire temperature interval, and also one value of ΔH_T. These data are used to plot the curve $\Delta C_p = \varphi(T)$, and then ΔH is determined for various temperatures by graphical integration (see Sec. 3.5.1). Next a curve $\Delta H = \varphi(T)$ is plotted, and according to it $\Delta G = \varphi(T)$. The ends of both curves are extrapolated to the region of very low temperatures (see Fig. 168).

Equation (13.35) can be obtained by expanding $\Delta H = \varphi(T)$ into a series and by other methods. For example, there is no need for the terms of the expansion to contain integral powers of T. Instead of beginning the expansion with the term containing T^2, we can begin with the term containing T^α (where $\alpha \neq 1$). This confirms the fact that we cannot proceed only from the first and second laws of thermodynamics to prove the heat law; Eq. (13.31) does not follow from them.

It is in this sense that we speak of the heat law as of the *third* law of thermodynamics.

Example 12. Find the temperature of transition of S(rhomb.) into S(mon.) if for this process $\Delta H = 50.4 + 3.69 \times 10^{-4} T^2$.

Solution. Since $\Delta G = 0$ at the point of transition, then from Eq. (13.36) we have $50.4 - 3.69 \times 10^{-4} T^2 = 0$, whence the transition temperature is 369.6 K or 96.4 °C (instead of the experimentally found value equal to 96 °C).

Such a problem can also be solved graphically. We get a figure similar to Fig. 168. According to the data in the initial conditions, both curves will begin (when $T = 0$) at the point $\Delta H = \Delta G = 50.4$. Next the curve $\Delta H = \varphi(T)$ will ascend, and the curve $\Delta G = \varphi(T)$

will descend, both curves being symmetrical. The point of intersection of the curve of ΔG with the axis of abscissas ($\Delta G = 0$) corresponds to the transition temperature. Below it, rhombic sulphur ($\Delta G > 0$) is stable, and above it monoclinic sulphur ($\Delta G < 0$).

Formula with Double Integrals. Table for Calculations. If we take Eq. (13.34) into account, then Eq. (5.26) for reactions in condensed systems becomes

$$\Delta G = -T\int_0^T \Delta H \frac{dT}{T^2}$$

(strictly speaking, the lower limit of integration cannot be indicated, because $\Delta G = 0$ when $T \neq 0$). Combining the latter equation with Eq. (13.35) written down in the form

$$\Delta H = \Delta H_0 + \int_0^T \Delta C_p dT \tag{13.37}$$

we get

$$\Delta G = \Delta H_0 - T\int_0^T \frac{dT}{T^2}\int_0^T \Delta C_p dT \tag{13.38}$$

Equations (13.37) and (13.38) are convenient for calculating ΔH and ΔG, because the integrals can be calculated beforehand according to the dependence of C_p on T. The values of the heat capacities down to very low temperatures have been used to compile tables (see, for example, [A26]) in which the values of

$$H_T - H_0 = \int_0^T C_p dT$$

$$\frac{G_T - G_0}{T} = -\int_0^T \frac{dT}{T^2}\int_0^T C_p dT$$

and

$$G_T - G_0 = -T\int_0^T \frac{dT}{T^2}\int_0^T C_p dT$$

are given for various substances.

The first integral is calculated according to a graph of $C_p = \varphi(T)$ and the second according to a graph of $\frac{1}{T^2}\int_0^T C_p dT = \varphi(T)$. For convenience, all the values in the tables are related to a gramme-atom.

If we know ΔH for a given temperature, it is not difficult to find the values of ΔH and ΔG for any temperature using these tables, in particular for a temperature sufficiently close to absolute zero, when the values of ΔH (and ΔG) do not lend themselves to direct measurement. Calculations by Eqs. (13.37) and (13.38) give more reliable results than by (13.35) and (13.36), because the power series of $C_p = \varphi(T)$ are not always accurate.

Example 13. Use the data given below, taken from reference tables, to calculate ΔG_{298} for the reaction

$$Fe + 2S(rhomb.) = FeS_2$$

and construct a graph of the temperature dependence of ΔG and ΔH from $T = 0$ to $T = 300$ K. Assume that the heat effect $\Delta H_{298} = -39\,000$ cal/mol.

T	20	50	100	200	250	280	290	300	320
Fe									
$H_T - H_0$	0.20	8.04	87.7	496	769	946	1007	1069	1195
$-(G_T - G_0)$	0.07	2.64	36.0	297	526	691	750	812	941
S(rhomb.)									
$H_T - H_0$	4.57	44.5	168	556	801	958	1012	1067	1178
$-(G_T - G_0)$	1.68	28.2	144	592	908	1112	1197	1274	1434
$\frac{1}{3}$ FeS_2									
$H_T - H_0$	0.08	2.73	42.5	323	534	672	720	769	867
$-(G_T - G_0)$	0.02	0.92	14.7	161	306	415	455	496	586

Solution. By interpolating the above data, from Eq. (13.37) we get $\Delta H_0 = -39\,000 - [3 \times 759 - (1056 + 2 \times 1056)] = -38\,109$ cal/mol. Next by Eq. (13.38) we get $\Delta G_{298} = -38\,109 - [3 \times 488 - (800 + 2 \times 1257)] = -36\,259$ cal/mol.

Inserting the tabulated values for different temperatures into Eqs. (13.37) and (13.38), we get the temperature dependence of ΔH and ΔG (see Fig. 168).

13.6.3. Gas and Heterogeneous Reactions

Accurate Solution. W. Nernst showed that the heat law can also be used for calculating gas and heterogeneous reactions. To do this, the relevant process should be conducted in a roundabout way

with the aid of a cycle consisting of reversible condensation of the reactants, the reaction between them in the condensed phase and reversible sublimation of the products.

Hence, after finding ΔG° (we omit the derivation) *, we get

$$\log K_p = -\frac{\Delta H_0^\circ}{4.576T} - \int_0^T \frac{\Delta C_p\, dT}{RT} + \Delta j \qquad (13.39)$$

where Δj is the algebraic sum of the so-called **true chemical constants** (see below).

If in accordance with Eq. (3.21), we divide the heat capacity of gaseous reagents into two components — $(C_p)_{\text{const}}$ not depending on the temperature and $(C_p)_{\varphi(T)}$ depending on it — after introducing the equation $\Delta H^\circ = \varphi(T)$ into Eq. (13.39), we have

$$\log K_p = -\frac{\Delta H_0^\circ}{4.576T} + \frac{(\Delta C_p)_{\text{const}}}{1.987}\log T + \\ + \frac{1}{4.576}\int_0^T \frac{dT}{T^2}\int_0^T (\Delta C_p)_{\varphi(T)}\, dT + \Delta j \qquad (13.40)$$

where ΔH_0° is the heat effect of the reaction reduced to absolute zero.

An accurate temperature dependence of the saturated vapour pressure corresponds to Eq. (13.40):

$$\log p = -\int_0^T \frac{\Delta H^\circ}{4.576}\frac{dT}{T^2} + j = -\frac{\Delta H_0^\circ}{4.576T} + \frac{(C_p)^{\text{g}}_{\text{const}}}{1.987}\log T + \\ + \frac{1}{4.576}\int_0^T \frac{dT}{T^2}\int_0^T [(C_p)_{\varphi(T)} - (C_p)^{\text{cl}}_{\text{const}}]\, dT + j \qquad (13.41)$$

which is obtained by integrating Eq. (7.2) and the expression $\Delta H^\circ = \varphi(T)$, the latter having the form of the equation

$$\Delta H^\circ = \Delta H_0^\circ + \int_0^T [(C_p)^{\text{g}} - (C_p)^{\text{cd}}_{\text{const}}]\, dT$$

with the following substitution of the quantity $(C_p)^{\text{g}}_{\text{const}} + (C_p)^{\text{g}}_{\varphi(T)}$ for $(C_p)^{\text{g}}$. Equation (13.41) coincides in form with the empirical equation (7.5).

---

* See, for example, [A26].

Comparing Eq. (13.39) with Eq. (13.20) and taking into account Eqs. (13.8) and (13.34), we find

$$I'' = \Delta j \quad \text{or} \quad I = -4.576\Delta j \tag{13.42}$$

i.e. the integration constant of the gas equilibrium equation equals the algebraic sum of the integration constants in vapour pressure equations (13.42), i.e. the true chemical constants.

The values of the chemical constants depend neither on the state of aggregation of the condensed phase, nor on the kind of crystal modification. Thus, for vapour of rhombic, monoclinic or liquid sulphur, the equation $p = \varphi(T)$ will contain the same constant.

The values of the double integrals in Eqs. (13.40) and (13.41) can be taken from tables compiled for each substance [A26] or from Appendices 5 and 6 using the data of Appendix 7.

It should be noted that if in Eqs. (13.40) and (13.41) the temperature dependence of the heat capacity of the reagents is assumed to be given by quantum formulas, in Eqs. (13.20) and (13.21) it is given by empirical power series, which are usually calculated according to data related to temperatures above 0 °C, i.e. they hold, as a rule, beginning from 0 °C. Therefore Eq. (13.42) will be absolutely accurate if quantum formulas are used in Eqs. (13.20) and (13.21). In other words, if the values of Δj corresponding to Eq. (13.40) are inserted in these equations, the values of $\log K_p$ will be generally somewhat "displaced", and to obtain correct values of $\log K_p$ the constant Δj will have to be replaced by a certain quantity that must be determined by trial and error.

The constants j are calculated either from experimental data, i.e. by Eq. (13.41) on the basis of the temperature dependence of the vapour pressure, the values of the heat capacities and the heats of phase transitions, or theoretically (Sec. 15.2). Table 15 gives the results of both methods of calculation.

Since the error in the values of j determined from experimental data is only several hundredths, as a rule, the discrepancy of most of the values of j should be considered as being within the limits of experimental errors. This confirms the truth of the heat law.

In addition, the coincidence of the integration constants I found according to the temperature dependence of the equilibrium constants with the algebraic sum of the true chemical constants found from the relationship $p = \varphi(T)$ by Eq. (13.41) proves the correctness of Eq. (13.42); this also confirms the truth of the heat law.

Example 14. Find the values of the true chemical constant for mercury if $T_m = 234.4$ K, $\Delta H_f = 555$, $\Delta H_{vap} = 14\,884$ cal/mol, $p_{234.4} = 2.67 \times 10^{-9}$, and according to tabulated data [A26] we have $H_{234.4} - H_0 = 1256$ and $(G_{234.4} - H_0)/234.4 = 8.34$ cal/mol·K.

Table 15. **True Chemical Constants of Selected Gases**

Gas	j		Gas	j	
	experimental by Eq. (13.41)	theoretical		experimental by Eq. (13.41)	theoretical
Ag	2.10	1.45	Br_2	2.57	2.47
Al	0.79	0.81	Cl_2	1.65	1.347
Ar	0.79	0.813	H_2	−3.68	−3.357
Au	1.00	1.11	I_2	3.08	3.03
Br	1.91	1.25	N_2	−0.153	−0.174
C	−0.79	—	O_2	0.547	0.533
Cd	1.50	1.488	CO	−0.075	0.041
Cl	1.44	0.73	CO_2	0.85	−0.830
Cu	1.00	1.11	HBr	0.24	0.20
He	−0.62	−0.68	HCl	−0.40	−0.419
Hg	1.83	1.866	HI	0.65	0.61
I	2.08	1.56	H_2O	−1.860	−1.775
K	1.10	1.0	H_2S	−0.918	−0.897
Mg	0.47	0.49	NH_3	−1.50	−1.55
Na	0.78	0.756	NO	0.55	0.550
Ne	0.396	—	N_2O	0.86	1.10
Pb	1.80	1.887	PH_3	−0.666	−0.662
Zn	1.21	1.135	CH_4	−1.941	−1.90

Solution. Since mercury vapour is monoatomic, $(C_p)^{g}_{const} = \frac{3}{2}R + R$ and $(C_p)_{\varphi(T)} = 0$. Therefore Eq. (13.41) becomes

$$\log p = -\frac{\Delta H_0^\circ}{4.576T} + 2.5 \log T - \frac{1}{4.576}\int_0^T \frac{dT}{T^2}\int_0^T C_p\, dT + j$$

We determine the enthalpy ΔH_0° for sublimation by Eq. (13.37), according to which

$$\Delta H_0^\circ = \Delta H_T^\circ - \int_0^T (C_p^g - C_p^{cd})\, dT$$

Since $C_p^g \neq \varphi(T)$, then

$$\Delta H_0^\circ = \Delta H_T^\circ - C_p^g T + \int_0^T C_p^{cd}\, dT$$

or

$$\Delta H_0^\circ = (14\,884 + 555) - 2.5R \times 234.4 + 1256 = 15\,531 \text{ cal/mol}$$

Hence by Eq. (13.41)

$$\log 2.67 \times 10^{-9} = -\frac{15\,532}{4.576 \times 234.4} + 2.5 \log 234.4 - \frac{8.34}{4.576} + j$$

whence $j = 1.83$, which differs from the theoretical value (Table 15) by less than 2%.

Approximate Solutions. Nernst simplified Eq. (13.40) and proposed the approximate equations

$$\log K_p = -\frac{\Delta H_0^\circ}{4.576T} + 1.75\,\Delta n \log T + \frac{\Delta b}{9.150}T + \Delta i \quad (13.43)$$

$$\log K_p = -\frac{\Delta H_{29}^\circ}{4.576T} + 1.75\,\Delta n \log T + \Delta i \quad (13.44)$$

where Δi is the algebraic sum of the so-called **conditional (empirical) chemical constants.**

He also proposed the equation

$$\Delta H_0^\circ = \Delta H_T^\circ - 3.5\,\Delta n T - \frac{1}{2}\Delta b T^2 \quad (13.45)$$

where (unlike the determination of Δb) only the gaseous components are taken into account in determining Δn.

Equation (13.43) is obtained from Eq. (13.40) by assuming a linear temperature dependence of the heat capacity of the reagents according to the empirical equation

$$C_p = 3.5 + bT \quad (13.46)$$

[This is why the values of ΔH_0° in Eqs. (13.40) and (13.43) differ from each other.] Equation (13.44) is obtained from the former if we substitute ΔH_{298}° for ΔH_0° and disregard the temperature dependence of the heat capacities. According to Eq. (13.46), the term $[(\Delta C_p)_{\text{const}}/1.987] \log T$ of Eq. (13.40) transforms into $(3.5\,\Delta n/1.987) \times \times \log T = 1.75\,\Delta n \log T$. At $\Delta n = 0$, Eqs. (13.43) and (13.44) become identical.

The conditional chemical constants i for selected gases are given in Table 16.

The values of i can be found either by trial and error, when the errors connected with the transition from Eq. (13.40) to Eqs. (13.43) and (13.44) must be compensated as far as possible, or by approxi-

Table 16. **Conditional Chemical Constants of Selected Gases**

Gas	i	Gas	i	Gas	i	Gas	i
Br	1.6	HBr	3.2	CO_2	3.2	C_2H_2	3.2
Cl	1.6	HCl	3.0	CS_2	3.1	C_2H_4	2.8
H	0.6	HF	3.4	HCN	3.8	C_2H_6	2.6
I	2.0	H_2	1.6	H_2O	3.6	C_6H_6	3.0
N	1.3	I_2	3.9	H_2S	3.0	C_2H_5OH	4.1
O	1.4	NO	3.5	H_2O	3.3	$(CH_3)_2O$	3.7
Br_2	3.2	N_2	2.6	SO_2	3.3	$(C_2H_5)_2O$	3.3
CO	3.5	O_2	2.8	NH_3	3.3	$CHCl_3$	3.2
Cl_2	3.1	S_2	2.8	CH_4	2.8	CCl_4	3.4

mate equations of the vapour pressure curve, i.e. in accordance with Eq. (13.43) by the equation

$$\log p = -\frac{\Delta H_0^\circ}{4.576T} + 1.75 \log T + \frac{b}{9.150} T + i \qquad (13.47)$$

and in accordance with Eq. (13.44) by the equation

$$\log p = -\frac{\Delta H_{298}^\circ}{4.576T} + 1.75 \log T + i \qquad (13.48)$$

The determination of i by Eq. (13.48) gives rough results, therefore the trial-and-error method is preferable in this case.

In the absence of data on the relationship $p = \varphi(T)$, the values of i can be approximately determined by the empirical formulas

$$i = 0.14 \frac{(\Delta H_{vap})_{n.b.p.}}{T_{n.b.p.}}; \quad i = 1.1a \text{ and } i = 1.761 \log p_{cr}$$

where a is a constant of the van der Waals equation.

It follows from the data of Table 16 that in the absence of values of the conditional constants, it can be assumed approximately that for monoatomic gases and H_2 they equal 1.5, and for all other gases 3. This facilitates calculations, because the only unknown quantity in Eq. (13.44), i.e. ΔH_{298}°, can be determined from the relevant tables according to Hess's law.

It should be understood that the conditional chemical constant i may be used only when calculating the equilibrium parameters by Eqs. (13.43) and (13.44), whereas calculations by Eq. (13.40) require that the true chemical constants be known [j differs from i not only in absolute value, but sometimes also in its sign (see Tables 15 and 16)].

If solids in addition to gases participate in a reaction, the above equations may be used; but in all the terms containing the heat capacity its components for the solid reagents must be introduced, remembering that $(C_p)_0 = 0$ and $j = 0$ for them.

Example 15. Calculate the equilibrium of the reaction

$$H_2O(g) = H_2 + \frac{1}{2}O_2$$

for the interval from 1000 to 3000 K (through every 500 kelvins) using (1) the accurate equation (13.40), and (2) the approximate equations [(a) (13.43) and (b) (13.44)].

Solution. 1. We calculate the value of ΔH_0° by Eq. (13.37), using the value of $\Delta H_{298}^\circ = 57\,796$ cal/mol (see Table 1). Since the value of T is small, the values of Θ/T are very great, and the last term of Eq. (3.21) is very small, hence Eq. (13.37) becomes

$$\Delta H_{298}^\circ = \Delta H_0^\circ + 298.2\Delta C_p$$

or

$$57\,796 = \Delta H_0^\circ + 298.2(6.96 + 0.5 \times 6.96 - 7.95)$$

whence $\Delta H_0^\circ = 57\,054$ cal/mol. The second term of Eq. (13.40) in accordance with Eq. (3.21) equals $1.253 \log T$. We calculate the third term containing the algebraic sum of the integrals $\int_0^T \frac{dT}{T^2} \int_0^T (C_p)_{\varphi(T)}\, dT$ according to the data given in Appendix 7. We determine the last term of the equation using Table 15:

$$\Delta j = [(-3.357) + 0.5 \times 0.533] - (-1.775) = -1.315$$

Thus, for the process of dissociation of water vapour (steam), Eq. (13.40) becomes

$$\log K_p = -\frac{12\,471}{T} + 1.253 \log T + \frac{1}{4.576}\left\{\int_0^T \frac{dT}{T^2}\int_0^T \varphi\left(\frac{6130}{T}\right)dT + \right.$$

$$+ \frac{1}{2}\int_0^T \frac{dT}{T^2}\int_0^T \varphi\left(\frac{2224}{T}\right)dT - \left[\int_0^T \frac{dT}{T^2}\int_0^T \varphi\left(\frac{2290}{T}\right)dT + \right.$$

$$\left.\left. + \int_0^T \frac{dT}{T^2}\int_0^T \varphi\left(\frac{5370}{T}\right)dT + \int_0^T \frac{dT}{T^2}\int_0^T \varphi\left(\frac{5510}{T}\right)dT\right]\right\} - 1.315 \quad \text{(a)}$$

We determine the values of the integrals from Appendix 5. For instance, for $T = 1000$ K, the quantity $\Theta/T = 2.224$ and

$$\int_0^T \frac{dT}{T^2} \int_0^T \varphi\left(\frac{2224}{T}\right) dT = 0.228$$

2. (a) We reduce the expressions $(C_p)_i = \varphi(T)$ (see Example 8, p. 452) to the form of Eq. (13.46). We choose $T = 1000$ K for these calculations, which gives

$$b = \frac{(C_p)_{1000} - 3.5}{1000}$$

Calculating b for H_2, O_2 and $H_2O(g)$, we get

$$(C_p)_{H_2} = 3.5 + 3.93 \times 10^{-3}T$$
$$(C_p)_{O_2} = 3.5 + 4.74 \times 10^{-3}T$$
$$(C_p)^g_{H_2O} = 3.5 + 6.21 \times 10^{-3}T$$

By Eq. (13.45)

$$\Delta H_0^\circ = 57\,796 - 3.5 \times 0.5 \times 298.2 - 0.5(3.93 + 0.5 \times 4.74 - 6.21)\, 10^{-3} \times 298.2^2 = 57\,270 \text{ cal/mol}$$

Equation (13.43) in accordance with the data of Table 15 becomes

$$\log K_p = -\frac{12\,519}{T} + 0.875 \log T + 0.009\,836 \times 10^{-3}T - 0.6 \quad \text{(b)}$$

(b) Equation (13.44) becomes

$$\log K_p = -\frac{12\,633}{T} + 0.875 \log T - 0.6 \quad \text{(c)}$$

The results of calculations by these equations are given below. Equation (d) is the same as Eq. (b), except that Δi has been taken equal to -0.12. The last line gives the most accurate values, a comparison with which gives a mean error of 0.3% for Eq. (a), 15.5% for (b), and 16.4% for (c). * The substitution of $\Delta i = -0.12$ for -0.6 [Eq. (d)] gives good results (the mean error drops to 1.1%).

T	1000	1500	2000	2500	3000
$-\log K_p$:					
by Eq. (a)	10.05	5.72	3.53	2.24	1.34
by Eq. (b)	10.50	6.18	3.99	2.66	1.76
by Eq. (c)	10.61	6.24	4.03	2.68	1.77
by Eq. (d)	10.13	5.76	3.55	2.20	1.29
according to experimental data	10.06	5.73	3.52	2.21	1.31

* The almost identical error of calculations by Eqs. (13.43) and (13.44) is due to the value of Δb being very small.

Example 16. 1. Find Eq. (13.44) for the processes of dissociation of carbonates ($p = 1$ atm). 2. Assess the accuracy of the equation obtained for the dissociation of $CaCO_3$ if the most authentic experimental data correspond to $T_{diss}=1167.6$ K. Can moist carbonate be dried in air at $T=1000$ K without a danger of its decomposition?

Solution. 1. From Eq. (13.44) and Table 16 it follows that

$$\log K_p = \log p_{CO_2} = 0 = -\frac{\Delta H^\circ_{298}}{4.576T} + 1.75 \log T + 3.2$$

This equation is shown graphically in Fig. 169.

2. We determine the value of ΔH°_{298} for the dissociation of $CaCO_3$ according to the heats of formation of the relevant substances (see Table 1):

$$\Delta H^\circ_{298} = (\Delta H^\circ_{298})_{CaO} + (\Delta H^\circ_{298})_{CO_2} - (\Delta H^\circ_{298})_{CaCO_3} = 42\,610 \text{ cal/mol}$$

Therefore in accordance with the found equation

$$\frac{9312}{T} = 1.75 \log T + 3.2$$

By consecutive approximations, we find $T_{diss} \approx 1100$ K, which differs from the experimentally found value by 67 kelvins.

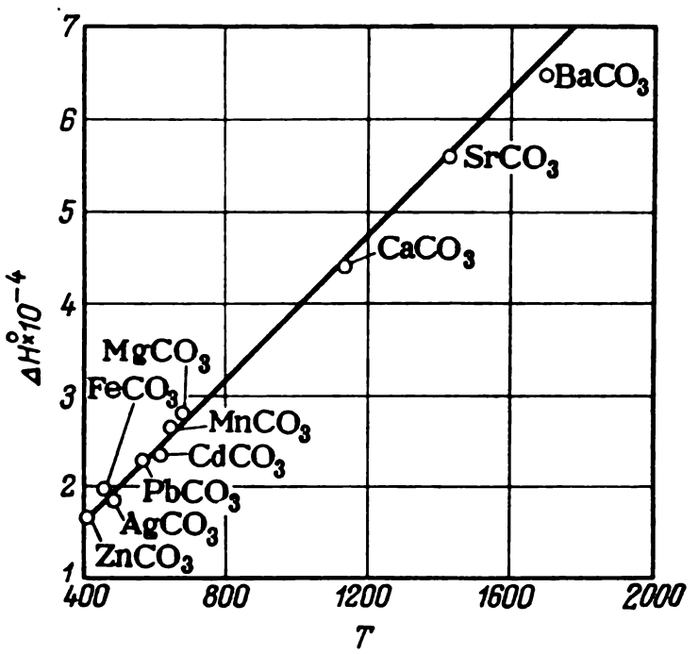


Fig. 169. Heats and temperatures of dissociation of selected carbonates.

Checking of Eq. (13.44). (See Example 16)

For $T = 1000$ K by the found equation $\log p = \varphi(T)$, we have

$$p_{CO_2} \approx 7.70 \times 10^{-2}$$

i.e. decomposition will occur in air. It can be avoided by either lowering the temperature or bringing the content of CO_2 in the gaseous phase up to about 10%.

Accuracy of Calculations. The following must be noted in appraising the above method of calculations: the accurate equation is cumbersome, requires numerous data which are often not available for its solution, and is very time consuming. The approximate equations are not accurate in the general case and can mainly be used only for rough calculations. This relates especially to Eq. (13.44). It was assumed in deriving it that the heat capacities of liquid and solid reagents equal zero, and that those of gases are constant and equal 3.5 for each component regardless of the temperature. Thus, in this equation, the third term of the accurate equation (13.40) disappears. Therefore, ignoring the temperature dependence of the heat capacity causes minimum errors when it concerns the reactants and the products to an equal extent. Hence, Eq. (13.44) is the most accurate if a reaction proceeds without a change in the number of moles, when the equation becomes a two-term one, i.e. coincides with Eq. (13.11). When $\Delta n = \pm 1$, the results of calculations are not always sufficiently reliable, while at $\Delta n = \pm 2$ and particularly at $\Delta n = \pm 3$ they may be unsatisfactory (it should be remembered that an error of one unit in the value of $\log K_p$ corresponds to an error of 10 units in the value of K_p).

If we sometimes succeed in accurately giving the temperature dependence of K_p even by means of Eq. (13.44), we usually achieve this by replacing the tabulated value of i with another one determined by trial and error. Consequently, in the absence of experimental data, we cannot predict the reliability of the results in each separate case. In addition, the errors of calculations grow together with the absolute value of the last term of Eq. (13.44).

In extrapolation to high temperatures, Eqs. (13.43) and (13.44) may give qualitatively unsatisfactory results, because, as A. Bachinsky showed (1928), the Nernst formula for the temperature dependence of the vapour pressure gives a drop in the pressure with a growth in the temperature for high temperatures.

At present, Eqs. (13.40), (13.43) and (13.44) are seldom used in calculating equilibrium, preference being given to a simpler and more accurate method whose fundamentals are set out below.

13.7. CALCULATING EQUILIBRIUM ACCORDING TO ABSOLUTE VALUES OF ENTROPY

13.7.1. Absolute Values of Entropy

Up to now, we have dealt only with *changes* in the properties of a system (H and C_p, G and S or correspondingly U and C_V, A and S). The absolute values of the heat capacity and entropy cannot be calculated by Eq. (13.32), i.e. they may have any (finite) values.

Nernst passed from the condition $\Delta C_p = 0$ [Eq. (13.32)] to the condition

$$\lim_{T \to 0} C_p = 0 \tag{13.49}$$

substantiating it by experimental data on the temperature dependence of the heat capacity and by the quantum theory of heat capacity (see Sec. 3.4.2).

M. Planck extended the heat law by transferring the condition $\Delta S = 0$ [Eq. (13.32)] from a system to a substance, i.e. by postulating that

$$\lim_{T \to 0} S = 0 \quad \text{or} \quad S_0 = 0 \tag{13.50}$$

The correctness of **Planck's postulate** can be explained by the following example. Upon the gradual cooling of a monocrystal (for instance NaCl), the thermodynamic probability P (See Sec. 4.3) sharply diminishes, and at $T = 0$, when all the ions are at the points of the crystal lattice, P will reach its minimum value, i.e. unity. Hence it follows that a given macrostate — the state of an *ideal* crystal at absolute zero — can be achieved by a single microstate, and in accordance with Eq. (4.26) the entropy becomes equal to zero. Equation (13.50) thus finds a clear interpretation.

The idea was advanced that an infinite increase in pressure should affect the magnitude of entropy in the same way as a decrease in temperature to absolute zero. This is mathematically clear, because it follows from Eq. (4.19) that $(\partial S/\partial p)_T < 0$, and therefore

$$\lim_{p \to \infty} S = 0$$

A number of authors, however, consider it unlikely that a substance at very high pressures will have the same properties as it would near absolute zero: at superhigh pressures the atoms of a substance will be so closely packed that their electron shells will overlap one another causing the temperature to rise.

Conversely, A. Kapustinsky (1945) on the basis of Eq. (4.19) advanced a new postulate. One of his proposed hypotheses states that upon compression of a pure solid phase to a "zero volume" (a superhigh pressure), the entropy becomes equal to zero, i.e.

$$\lim_{V \to V_0} S = 0$$

It should be noted in passing that the analogy between the behaviour of a substance at $T \to 0$ and $p \to \infty$ may also tell us that at both superlow temperatures and superhigh pressures substances form many modifications. For instance, up to 11 modifications were discovered in camphor up to $p = 35\,000$ atm.

Nernst's and Planck's postulates are sometimes combined under the general name of the "third law of thermodynamics", but this does not mean that an equality sign is placed between them.

Notwithstanding the great significance of the third law, it is inferior to the first and second laws of thermodynamics in its general nature. Unlike them, the third law does not lead to the determination of any fundamental quantities such as energy (the first law), entropy and absolute temperature (the second law), but only limits the magnitude of one of them in accordance with Eq. (13.50).

The latter can be written down in the form

$$\lim_{T \to 0} \left(\frac{\partial G}{\partial T} \right) = \lim_{T \to 0} \left(\frac{\partial H}{\partial T} \right) = 0 \tag{13.51}$$

which is a special case of the equation

$$\lim_{T \to 0} \left(\frac{\partial X}{\partial T} \right)_x = 0 \tag{13.52}$$

where X = generalized force
x = generalized path (see Sec. 5.3).

In particular, if $X = p$ and accordingly $x = V$, Eq. (13.52) becomes

$$\lim_{T \to 0} \left(\frac{\partial p}{\partial T} \right)_V = 0$$

which follows from a combination of Eqs. (13.50) and (4.18).

It also follows from Eq. (13.50) that

$$\lim_{T \to 0} \left(\frac{\partial S}{\partial p} \right)_T = 0$$

and in accordance with Eq. (4.19)

$$\lim_{T \to 0} \left(\frac{\partial V}{\partial T} \right)_p = 0$$

In other words, a change in the temperature of a body near absolute zero at V = const does not result in a change in pressure, and at p = const, a change in volume, i.e. does not result in any work of expansion or compression.

All this permits us to conclude that *a number of properties of a condensed phase* (G, H, A, V, C_p, C_V, the thermal expansion coefficients, electrical conductivity, etc.) *stop depending on the temperature near absolute zero.*

It follows from this conclusion that when the temperature is still approaching absolute zero, substances acquire such properties that it is in principle impossible to reach the absolute zero of temperature. Indeed, when absolute zero is approached sufficiently closely,

the heat capacity of a substance becomes negligible, and as a result absolute zero cannot be reached by the removal of heat.

M. Lomonosov already predicted the presence of a minimum temperature. He pointed to the existence of "...the greatest and last stage of cold consisting in the complete rest of particles."*

In formulating the principle of unattainability of absolute zero, various authors often proceed, as for the first and second laws of thermodynamics, from the impossibility of a perpetual motion machine (of the third kind) : *it is impossible to construct a machine that would work by cooling a body to absolute zero.*

Progress in engineering makes it possible to achieve lower and lower temperatures (at present cooling to 10^{-6} K has been achieved) **, but this does not at all mean that it will ever be possible to reach absolute zero.

Calculation of Absolute Values of Entropy. Equation (13.50) allows us to calculate the *absolute* value of entropy. The need to choose a hypothetical origin from which to count this function now disappears. Indeed, by integrating Eq. (4.21) within the limits from $T = 0$ to T, we get the equation

$$S_T - S_0 = \int_0^T \frac{C_p}{T} dT$$

which in connection with Eq. (13.50) becomes

$$S_T = \int_0^T \frac{C_p}{T} dT = \int_{-\infty}^{\ln T} C_p d \ln T = 2.303 \int_{-\infty}^{\log T} C_p d \log T \quad (13.53)$$

An analysis of this equation shows that if Eq. (13.49), which is confirmed by experimental data and the quantum theory, were not true, the entropy would tend to infinity, which contradicts Eq. (13.50).

The absolute value of the entropy in accordance with Eq. (13.53) is calculated by the equation

$$S_T = \int_0^{T_{\text{I-II}}} \frac{(C_p)_{\text{I}}^{\text{c}}}{T} dT + \frac{\Delta H_{\text{I-II}}}{T_{\text{I-II}}} + \int_{T_{\text{I-II}}}^{T_{\text{m}}} \frac{(C_p)_{\text{II}}^{\text{c}}}{T} dT +$$

$$+ \frac{\Delta H_{\text{f}}}{T_{\text{m}}} + \int_{T_{\text{m}}}^{T_{\text{b}}} \frac{C_p^{\text{liq}}}{T} dT + \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} + \int_{T_{\text{b}}}^{T} \frac{C_p^{\text{g}}}{T} dT \quad (13.54)$$

* Lomonosov, M. V. *Polnoe sobranie sochinenii* (Collected Works) in 10 volumes, Vol. 2, p. 39. Moscow, AN SSSR (1951).

** By means of adiabatic demagnetization of nuclear-magnetic substances.

The first term equals the entropy of a solid (crystalline) substance at the temperature $T_{I\text{-}II}$ of its transition from one modification to another; the second term corresponds to the change in entropy upon a phase transition; the third to the increase in entropy when the substance is heated from the transition temperature I-II to the melting point T_m; the fourth term is the change in entropy in melting, and so on. If a substance has only one crystal modification, the first three terms of the equation are replaced with an integral corresponding to the entropy of the solid substance at its melting point. Conversely, if there are several modifications, the number of terms grows correspondingly. When a substance whose entropy is to be determined is not in the gaseous state at a given temperature, but in the liquid or solid state, the corresponding terms will disappear in Eq. (13.54). For example, when calculating S_{300} for H_2O, the last two terms will be deleted in Eq. (13.54), and the upper limit of the next-to-last integral will become equal to 300 K.

Since in the majority of cases the values of $C_p = \varphi(T)$ are known beginning only from $T \approx 90$ K (and from 10-20 K if cooling is conducted with the aid of liquid hydrogen), * it becomes necessary to divide the first term of Eq. (13.54) into two integrals. The value of the first (taken within the interval from $T = 0$ to the temperature T' for which the values of the heat capacity are already known) is calculated either with the aid of data given in Appendix 6, or by graphical extrapolation of the heat capacity curve, or, finally, by specially developed methods (see, for example, [B79] and [D47]).

The entropy of solid substances for a temperature beginning from which experimental data have been obtained can also be calculated by extrapolation on the basis of Eqs. (3.17) or (3.18) and (3.19). For instance, for a "three-dimensional" crystal

$$S_{T'} = \int_0^{T'} \frac{C_p}{T} dT \approx \frac{(C_p)_{T'}}{3} \approx \frac{(C_V)_{T'}}{3} \qquad (13.55)$$

To date, general mathematical relationships between C_p and T (except for very low temperatures) have not been found, and the integrals in Eq. (13.54) are determined from graphs of $C_p/T = \varphi(T)$ or $C_p = \varphi(\log T)$ (Fig. 170). Even when the value of the entropy can be found with the aid of theoretical equations of the heat capacities or with the aid of the corresponding functions (Appendices 5 and 6), the graphical method of calculations is nevertheless the most reliable. Its result does not depend on the accuracy of any equation, whereas, for example, calculations by Eq. (3.17) for elevated temper-

* Only in recent decades have measurements of the heat capacity beginning from about 0.1 K been successful.

atures give results that are not very satisfactory, while for non-crystalline bodies they are unreliable even for low temperatures.

Calculations by means of the graph $C_p = \varphi(\log T)$ owing to the impossibility of extrapolating the curve over a great distance

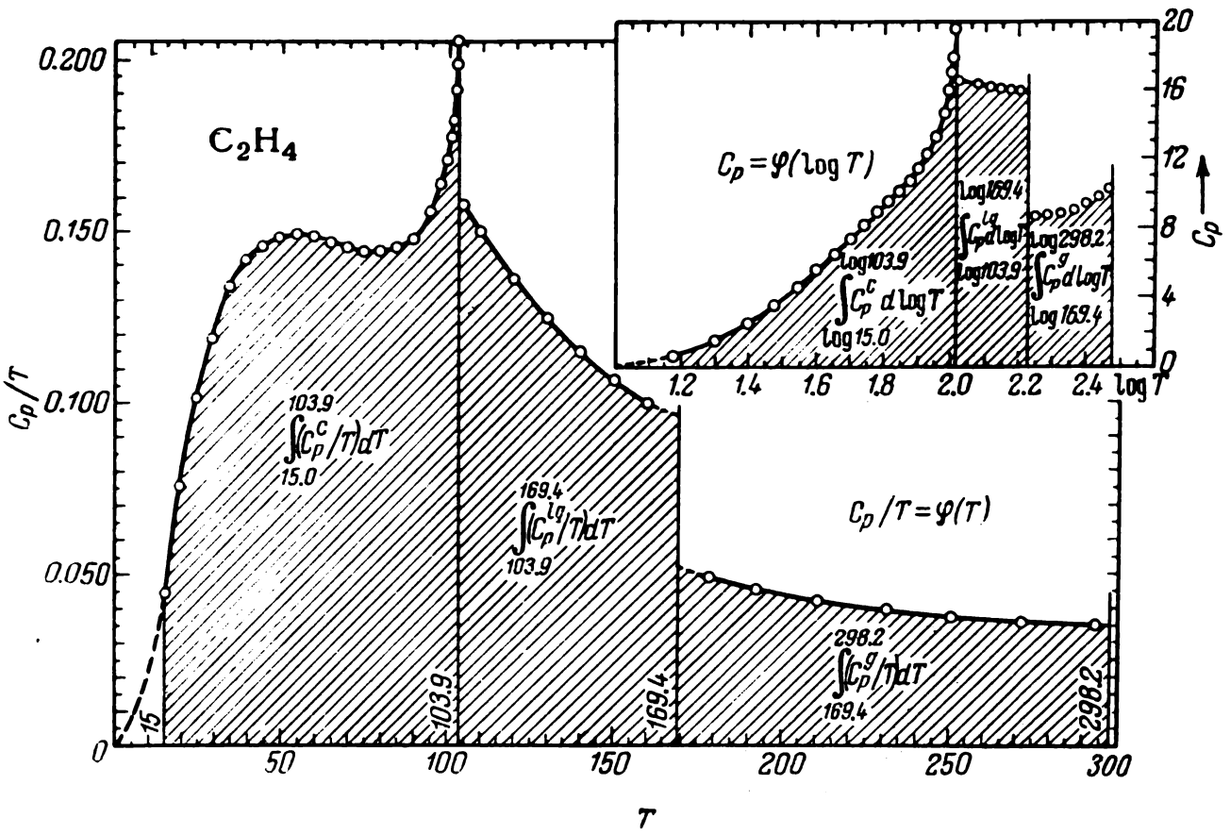


Fig. 170. Graphical method of calculating entropy.
(See Example 17)

($\lim_{T\to 0} \log C_p = -\infty$) are somewhat inaccurate (lower results), but for a low temperature, when the heat capacity rapidly diminishes to zero, the error is negligible.

Calculation of the absolute entropy of a substance will be considered in Example 17.

Limitations of Planck's Postulate. Consider the states of substances for which even at $T=0$ the thermodynamic probability is greater than unity and, therefore, $S_0 > 0$. This is possible when a given substance is a solution or a mixture, forms a metastable crystal modification, is vitreous or has an unordered crystalline structure; certain other cases are also known.

In all the states listed above, there is a certain disorderliness in the structure. If it is retained down to absolute zero, a **zero (residual) entropy** also appears whose magnitude can be assessed in the majority of cases.

Assume that a given substance, which is a mixture, can be considered as an ideal solution. According to Eqs. (5.24) and (8.48),

the formation of an ideal solution at any temperature is attended by a change in entropy equal to $-R\sum x_i \ln x_i$. Assume further that we cooled this solution, and it remained ideal down to $T = 0$ K (to prevent decomposition into its constituent parts, the solution should be cooled very rapidly). Hence, considering for each component that $(S_0)_i = 0$, we get for the solution $S_0 = -R\sum x_i \ln x_i$. For instance, for a binary solution for which $x_1 = 0.272$ we have

$$S_0 = -4.576(0.272 \log 0.272 + 0.728 \log 0.728) = 1.16$$

which agrees with the value 1.03 ± 0.15 e.u. found on the basis of experimental data (for a mixture of AgCl and AgBr containing 27.2 mole per cent of AgCl).

Should a liquid become vitreous upon solidification, the curve $C_p/T = \varphi(T)$ does not break at the melting point (see Fig. 170). Therefore, other conditions being equal, the entropy of glass is greater than that of a crystalline body by the quantity

$$\Delta S_0 = \int_0^{T_m} \left(\frac{C_p^{gl}}{T} - \frac{C_p^c}{T} \right) dT + \frac{\Delta H_f}{T_m}$$

The first term of the right-hand side of this equation equals the shaded area in Fig. 171. Representatives of such substances are ethanol and glycerine, for which S_0 equals 2.6 and 4.6 e.u., respectively.

If a substance forms a metastable crystalline modification when cooled (this can be illustrated by a graph similar to Fig. 171 on the condition that $T_m = T_{tr}$, while the lower and upper curves characterize the stable and unstable modifications, respectively), then

$$\Delta S_{tr} = \int_0^{T_{tr}} \left[\frac{(C_p^c)_{unst}}{T} - \frac{(C_p^c)_{st}}{T} \right] dT + \frac{\Delta H_{tr}}{T_{tr}}$$

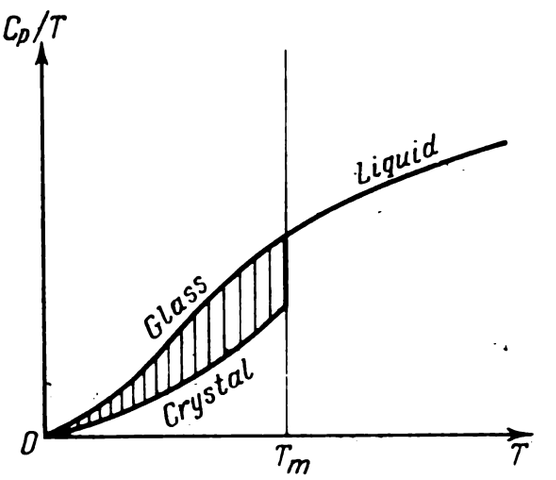


Fig. 171. Illustrating the graphical method of calculating entropy

The quantity ΔS_{tr} equals the shaded area in Fig. 171. For example for phosphorus ($T_{tr} = 49.34$), the term containing the integral equals 3.748 e.u., and $\Delta S_{tr} = 3.757$ e.u.

In addition to these two cases due to supercooling of the phases, and also to possible violation of the proper structure of a solid,

the disordered structure of crystals may also be a source of distortions, because when a crystal is cooled to very low temperatures, the orientation hindrance becomes so significant that the molecules may not have time to become arranged orderly during cooling. In other words, the "disorderliness" appearing at elevated temperatures under the influence of the energy of thermal motion does not vanish without a trace at low temperatures, because the possibilities of motion diminish so rapidly that order does not set in. Consequently, the substance at all stages of cooling will not be in the stable equilibrium corresponding to a minimum of the Gibbs energy.

Thus, at $T = 0$ we get a crystal characterized by the presence of several orientations of equal (minimum) energy. Considering such a crystal as an ideal solid solution, we can assume that the zero entropy equals the entropy of mixing of the different kinds of its particles.

For example, if we consider the two orientations of CO molecules (C=O, O=C), owing to the approximate equivalence from the energy viewpoint of their carbon and oxygen ends to be equally probable not only at ordinary, but also at low temperatures, the zero entropy of carbon monoxide should equal $-4.576\ (0.5 \log 0.5 + 0.5 \log 0.5) = 1.377$ e.u. The difference between the values of the absolute (found on the basis of spectroscopic data) and calorimetric entropies for CO at $T = 298$ K was found to equal 1.10 e.u.; for the linear molecules N_2O and NO similar to CO it was found to equal 1.14 and 0.75 e.u., respectively. *

In addition to those listed above, there are also other sources of zero entropy (the presence of isotopes, nuclear spin and uneven distribution of the molecules between the energy levels) that are treated in Chap. 15. Here we shall only indicate that zero entropy due to the isotope effect can be taken into account quantitatively if we consider a mixture of isotopes to be an ideal solution. The entropy of nuclear spin manifests itself in molecules whose atoms have nuclear spin. Molecules exist (including hydrogen and deuterium) in which the effect of disorderliness is superposed onto the nuclear spin effect. For example when hydrogen is cooled, ortho-hydrogen should transform into para-hydrogen. The per cent

* A result of the disordered arrangement of the molecules in crystals of non-linear molecules of H_2O and D_2O is the presence of a zero entropy equal to 0.83 and 0.69 e.u., respectively. If we take such linear molecules as HCN, then because of the sharp difference between the properties of hydrogen and nitrogen atoms almost complete orderliness will be observed down to low temperatures, and for such substances $S_0 \approx 0$.

of para-hydrogen in an equilibrium mixture of para- and ortho-hydrogen is indicated below

T	273	250	200	150	100	75	50	40	30	20	0
[para-H_2], % ...	25.13	25.24	25.90	28.54	38.51	51.86	76.89	88.61	96.98	99.82	100.0

The rate of this process drops with lowering of the temperature in the absence of a suitable catalyst, however, consequently at $T = 0$ hydrogen is a hindered system (a solid solution of both forms).

Table 17 gives the differences between the values of the spectroscopic and calorimetric entropies for $T = 298.2$ K for H_2, D_2, H_2O and D_2O, as well as the theoretical values of S_0°.

Table 17. **Entropies of H_2, D_2, H_2O and D_2O Found from Calorimetric and Spectroscopic Data**

Substance	$(S^\circ_{298})_{sp}$	$(S^\circ_{298})_{cal}$	ΔS°_{298}	$(S^\circ_0)_{theor}$
H_2	33.979	29.69	4.29	4.390
D_2	38.731	33.65	5.08	5.093
H_2O	47.848	44.28	3.66	3.787
D_2O	46.66	45.89	0.77	0.77

The differences between the values of S_0 found as a result of calorimetric measurements (p. 478) and theoretical calculations (see Chap. 15) indicate first of all a certain orderliness of the structure, i.e. the predominance of one of the forms. The difference between the values always has the same sign, because the heat capacities used to calculate the calorimetric entropies for temperatures close to absolute zero are less than those that should be the rule in the presence of unhindered equilibrium.

The numerous limitations of Planck's postulate do not at all mean that the calculation of absolute entropies considered in the preceding section loses its meaning. Even if we do not take these limitations into account in those very few cases when they reach considerable values, the discrepancies in S and ΔS will be of the order of R entropy units, which when reduced to ΔG is a value that as a rule is within the limits of accuracy of the heat effects. The errors due to such constantly acting factors as the isotope effect and nuclear spin mutually cancel each other in determining ΔS for

a reaction, because the same atoms are constituent parts of both the reactants and the products. *

Standard Entropies. Calculation of equilibrium (see Sec. 13.7.2) is considerably simplified owing to the availability of tables of the values of S°_{298} (for similar tables of ΔH°_{298} and ΔG°_{298} see Secs. 3.2 and 13.4.2, respectively) found in one of the following ways.

1. By Eq. (13.54), the last term of which equals

$$\int_{T_{ph.tr}}^{298.2} \frac{C_p}{T} dT$$

with reduction for gases to the standard state according to the equation written down for the boiling point

$$S^\circ_T = S_T + \frac{27}{32} \frac{RT^3_{cr}}{T^3} \frac{p}{p_{cr}} \qquad (13.56)$$

which is obtained by combining Eqs. (5.20) and (4.19).

The correction expressed by Eq. (13.56) is generally of the order of magnitude of 0.1 e.u. and may be ignored in approximate calculations.

The values of S°_{298} for compounds in the state of an ideal gas (when substances are in the liquid or solid states at 25 °C) are calculated by the equation

$$(S^g_{298})^\circ = S^{lq}_{298} + \frac{(\Delta H_{vap})_{298}}{298.2} + \frac{27RT^3_{cr}p_{298}}{32 \times 298.2^3 p_{cr}} - R \ln \frac{1}{p_{298}} \qquad (13.57)$$

The values of S°_{298} for ions (in an aqueous solution) unlike other standard entropy values are not absolute. They are related to the standard entropy of a hydrogen ion taken equal to zero. This convention falls away if we calculate the total entropy of the ions which a chemical compound decomposes into. For example, the quantity

$$2(S^\circ_{298})_{K^+} + (S^\circ_{298})_{CO_3^{2-}} = 2 \times 24.12 + (-13.6) = 34.64 \text{ e.u.}$$

is the absolute entropy of potassium carbonate in an aqueous solution in the standard state upon its complete dissociation.

---

* Exceptions are processes of isotope exchange and low-temperature reactions in which hydrogen (below 0 °C) or deuterium (below −70 °C) participates.

2. On the basis of statistical methods using a model of a molecule and spectroscopic data (see Chap. 15).

3. Using indirect methods of calculations, for example on the basis of values of ΔG°_{298} and ΔH°_{298} in combination with known values of S°_{298}, i.e. by Eq. (5.22).

4. By approximate methods of calculation (see pp. 491ff).

At present the values of S°_{298} (not counting estimated ones) are known for over 2500 substances.

A summary of standard entropies is given in Tables 18 and 19 and in Appendix 2.

Table 18. **Standard Entropies of Selected Substances** *

Substance	S°_{298}	Substance	S°_{298}
Ba(c)	16.0**	H_2O(g)	45.106
Br_2(g)	58.645	H_2O(lq)	16.75
C (diamond)	0.566	KBr(c)	22.93
C (graphite)	1.372	KCl(c)	19.73
CO(g)	47.214	K_2CrO_4(c)	46.2**
C_2H_5COOH(lq)	51.0***	MgS(c)	10.6**
C_2H_5OH(g)	67.5	NO(g)	50.33
C_2H_6(g)	54.85	NOCl(g)	62.53
C_6H_6(g)	64.34	NaCl(c)	17.24
CaS(c)	13.5	NaI(c)	24.0***
$CaSiO_3$(c)	19.6	Na_2SiO_3(c)	27.21
Ca_2TiO_4(c)	31****	S_2(g)	54.50
$FeCl_2$(c)	28.2	Sn(c), grey	10.55
Fe_3O_4(c)	34.94	SrS(c)	17.0**
H_2(g)	31.195	$ZnCl_2$(c)	26.64

* See also Table 19 and Appendix 2.
** Calculated by Kireev's method (see p. 491).
*** Calculated by Eq. (13.70) with $Y = C_p$.
**** Calculated by Eq. (13.69).

Table 19 compares the standard entropies calculated by Eqs. (13.54) and (13.56) with those found theoretically on the basis of statistical methods. The correctness of both methods of calculation is confirmed by coincidence of the data contained in the table within the limits of the error tolerated in determining them.

Table 19. **Standard Entropies of Selected Gases Calculated by Thermodynamic and Statistical (Spectroscopic) Methods**

Gas	S°_{298}		Gas	S°_{298}	
	thermodynamic	spectroscopic		thermodynamic	spectroscopic
Ar	36.95 ± 0.2	36.99 ± 0.01	HBr	47.63 ± 0.15	47.46 ± 0.05
Kr	39.17 ± 0.10	39.20 ± 0.01	HCN	47.98 ± 0.2	48.21 ± 0.10
Ne	35.01 ± 0.10	34.95 ± 0.01	HCl	44.47 ± 0.15	44.64 ± 0.05
Xe	40.7 ± 0.3	40.54 ± 0.01	HI	49.48 ± 0.15	49.35 ± 0.05
Cl_2	53.31 ± 0.10	53.29 ± 0.01	H_2S	49.10 ± 0.10	49.18 ± 0.10
N_2	45.93 ± 0.15	45.77 ± 0.01	NH_3	45.96 ± 0.10	46.03 ± 0.03
O_2	49.10 ± 0.10	49.00 ± 0.01	PH_3	50.35 ± 0.10	50.37 ± 0.2
CO	46.2	47.21 ± 0.01	SO_2	59.24 ± 0.10	59.29 ± 0.15
CO_2	51.11 ± 0.10	51.07 ± 0.05	CH_4	44.45 ± 0.2	44.52 ± 0.10
COS	55.27 ± 0.10	55.32 ± 0.10	C_2H_4	52.48	52.45

Example 17. Use the data given below to calculate the standard entropy of ethene :

T	C_p	T	C_p	T	C_p
15	0.682	80	11.55	120	16.32
20	1.519	85	12.35	130	16.21
25	2.537	90	13.29	140	16.12
30	3.559	95	14.73	150	16.07
35	4.682	98.1	16.03	160	16.04
40	5.665	100	17.05	169.4***	3237****
45	5.542	101.4	17.97	179.6	8.786
50	7.394	102.3	18.59	192.8	8.807
55	8.211	103.0	19.62	210.8	8.930
60	8.923	103.6	20.58	231.4	9.177
65	9.553	103.9*	800.8**	250.9	9.464
70	10.18	105	16.54	272.1	9.910
75	10.83	110	16.46	293.5	10.337

* T_m.
** ΔH_f.
*** T_b.
**** ΔH_{vap}.

Solution. The entropy of ethene by Eq. (13.54) is

$$S^{g}_{298} = \int_{0}^{15} \frac{(C_p)^{c}_{C_2H_4}}{T} dT + \int_{15}^{103.9} \frac{(C_p)^{c}_{C_2H_4}}{T} dT + \frac{800.8}{103.9} +$$

$$+ \int_{103.9}^{169.4} \frac{(C_p)^{lq}_{C_2H_4}}{T} dT + \frac{3237}{169.4} + \int_{169.4}^{298.2} \frac{(C_p)^{g}_{C_2H_4}}{T} dT$$

We find the integral terms by constructing a graph in the coordinates $C_p/T = \varphi(T)$ (see Fig. 170), for which we use the above values of C_p to calculate C_p/T.

The first integral obtained from the graph by extrapolation gives $S_{15.0} = 0.24$ [calculation by Eq. (13.55) gives $S_{15.0} = 0.23$, extrapolation by Eq. (3.17) ($\Theta = 130$) gives $S_{15.0} = 0.25$]. As a result we have:

$S^{c}_{15.0} - S^{c}_{0}$, extrapolation	0.24
$S^{c}_{103.9} - S^{c}_{15.0}$, graphical integration	12.21
$\Delta S_m = S^{lq}_{103.9} - S^{c}_{103.9} = 800.8/103.9$	7.70
$S^{lq}_{169.4} - S^{lq}_{103.9}$, graphical integration	7.91
$\Delta S_{vap} = S^{g}_{169.4} - S^{lq}_{169.4} = 3237/169.4$	19.11
$(S^{g}_{169.4})^{\circ} - S^{g}_{169.4} = \dfrac{27 \times 1.987 \times 282.4^3 \times 1}{32 \times 169.4^3 \times 50.0}$	0.16
$S^{g}_{298.2} - S^{g}_{169.4}$, graphical integration	5.12
S°_{298}	52.45 e.u.

The sum of the first five terms (47.17 e.u.) gives the entropy of ethene in the state of a real gas at the boiling point. The sixth addend corresponds to a correction for the deviation of C_2H_4 from the state of an ideal gas; it is determined by Eq. (13.56) (the critical parameters were taken from Appendix 9). Thus, the sum of the first six terms equals the entropy of ethene in the state of an ideal gas at $p = 1$ atm and $T = 169.4$ K.

Entropy and the Nature of a Substance. The introduction of standard entropies made it possible to raise the problem of the relationship between the entropy and features of substances, because the difference between the values of S°_{298} (or S°_{T}) reflects (for the same

state of aggregation) only the difference in the nature of substances. A few examples follow.

The entropy in the series El_n, $MeHal_n$, $A \cdot nH_2O$ and similar related series of substances grows with increasing molecular weight. Examples are the series Se(g) ($S^\circ_{298} = 42.212$ e.u.), Se_2(g) (60.22) *, and Se_6 (g) (about 110); and the series $PtBr_2$(c) (12.77), $PtBr_3$(c) (26.60), and $PtBr_4$(c) (39.09). The entropy grows in homologous series of organic compounds.

It follows from Eq. (4.26) that, other conditions being equal, S°_{298} should diminish with a growth in the hardness of a substance, i.e. in the interatomic attraction in it. For instance, $S_{Cs(c)}$ (20.16) $\gg$ $\gg S_{W(c)}$ (7.80).

The dependence of S°_T (and in particular of S°_{298}) on the nature of a substance most clearly manifests itself when considering inorganic substances from the standpoint of Mendeleev's Periodic Table of the Elements. A general picture of the periodicity is given by a graph like that shown in Fig. 172. In this case, in view of the sensitivity of the values of S to the state of aggregation of a substance ($S^g \gg S^{lq} > S^c$) it is distorted somewhat by the circumstance that some chlorides in standard conditions are liquids (for example $SiCl_4$), and some are gases (for example HCl). The result is an increase (especially sharp for gaseous substances) in the values of S°_{298}, i.e. an upward displacement of the corresponding points in Fig. 172. In a series of similar substances S°_{298} in a subgroup grows (Fig. 173). Within a period, the change in S°_{298} may be more complicated. This can be seen by Fig. 174; the transition from soft lithium to superhard diamond is attended by a drop in S°_{298} (although the atomic weight grows), next in connection with the gaseous state of the following elements S°_{298} sharply grows. (From the values of S°_{298} given in this figure for the elements of subgroup VIIA it follows that hydrogen is to some extent an analogue of the halogens.) The similarity of substances due to the relevant arrangement of the elements forming them in the periodic table also manifests itself in the closeness of the standard entropies of these substances. Thus, S°_{AlN} (about 4.8) $\approx S^\circ_C$ (0.566) $+ S^\circ_{Si}$ (4.50), S°_{InAs} (about 20) $\approx$ $\approx S^\circ_{Ge}$ (7.44) $+ S^\circ_{Sn}$ (12.32). Such approximate equations are the more accurate, the closer are the substances being compared in their structure (and hardness).

Let us turn to organic compounds. The sensitivity of entropy to structure manifests itself especially vividly, in particular owing to the fact that ordering of the structure (a great symmetry) of the

* Here and further the figures in parentheses give the values of S°_{298} in entropy units.

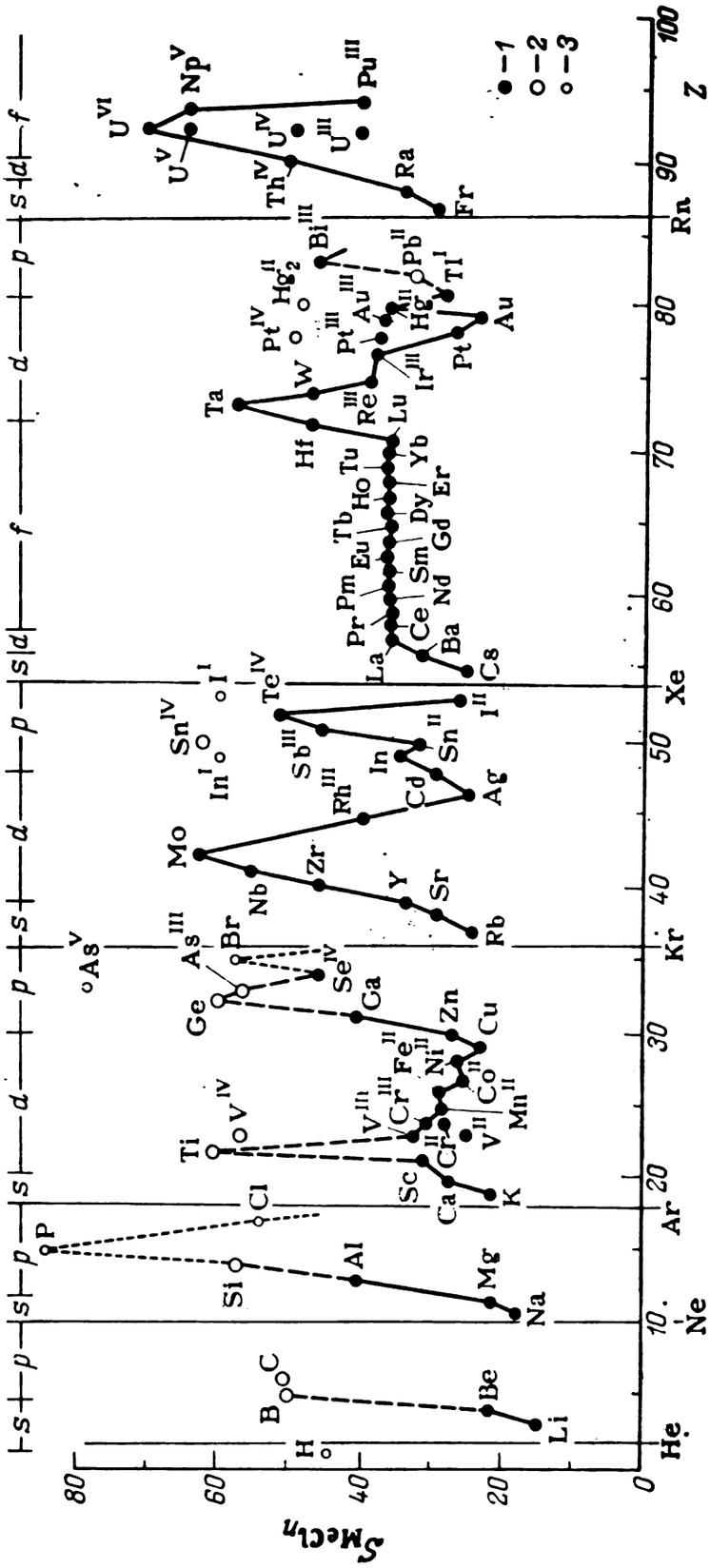


Fig. 172. Dependence of standard entropies S°_{298} of chlorides on atomic number of element:

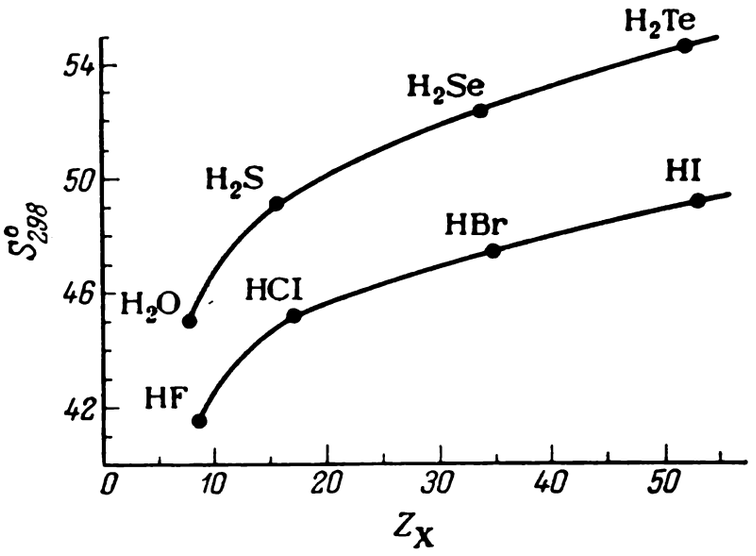


Fig. 173. Dependence of standard entropies of H_2X (X = O, S, Se or Te) and HX(X=F, Cl, Br or I) on Z_X

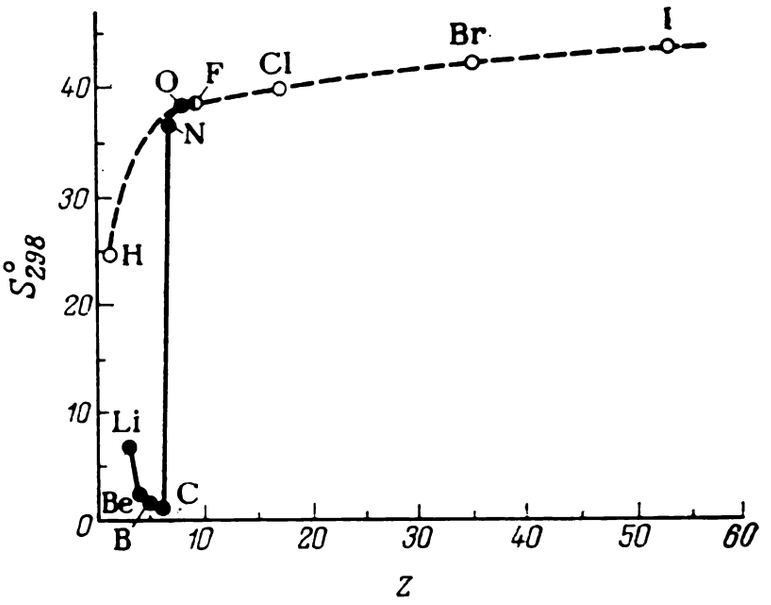


Fig. 174. Dependence of standard entropies of elements of 2nd period (solid line) and subgroup VIIA (dashed line) on atomic number

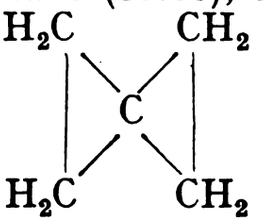
molecules results in decreasing of the entropy. Two examples are given below:

$$CH_3-(CH_2)_5-CH_3(lq) \qquad (78.5)$$

$$\begin{array}{l} \quad CH_3 \\ \quad | \\ CH_3-C-CH_2-CH_3(lq) \\ \quad | \\ \quad CH_3 \end{array} \qquad (71.6)$$

$$CH=CH-CH_2-CH_2-CH_3(lq) \qquad (63.8)$$

$$\begin{array}{l} \quad CH_2 \\ \quad\diagup\quad\diagdown \\ H_2C \quad CH_2(lq) \\ \quad | \quad\quad | \\ H_2C-\!-CH_2 \end{array} \qquad (48.8)$$

In the series of gaseous substances *n*-pentane (83.40), 1-pentene (82.65), 1-pentine (78.82) and spiropentane  (67.45),

the entropy diminishes not so much as a result of the reduction of the number of hydrogen atoms as because of the growth in the number of double and triple bonds — this imparts a more rigid structure to a molecule. It is natural that the decrease is especially appreciable when passing from pentine to spiropentane.

Some Approximate Methods of Calculating Entropy. The availability of values of S°_{298} for a great number of various substances makes it possible to discover certain laws. This allows us to extend the amount of data without resorting to direct measurement of equilibrium and time-consuming calorimetric measurements at low temperatures. Below are given some equations for calculating the standard entropy of inorganic and organic compounds (for simplification the symbol S° or S is generally used instead of S°_{298}).

Inorganic Substances. V. Kireev's method (1947) bases the calculation of S° on : (1) ΔS°_a — the entropy of formation of a compound from its elements in the hypothetical state of a monoatomic ideal gas at the given pressure and temperature ; and (2) ΔS°_i — the entropy of formation of compounds from their elements on the condition that both the elements and the compounds are in the state of an ideal gas (for the elements — a monoatomic gas).

Consequently

$$\Delta S^\circ_a = S^\circ - \Sigma n_{el} (S^\circ_{el})_i \qquad (13.58)$$

and

$$\Delta S^\circ_i = S^\circ_i - \Sigma n_{el} (S^\circ_{el})_i \qquad (13.59)$$

The relationship between ΔS°, ΔS°_a and ΔS°_i is given by the expression

$$\Delta S^\circ = \Delta S^\circ_a - [\Sigma n_{el} S^\circ_{el} - \Sigma n_{el} (S^\circ_{el})_i] =$$
$$= \Delta S^\circ_i + (S^\circ - S^\circ_i) - [\Sigma n_{el} S^\circ_{el} - \Sigma n_{el} (S^\circ_{el})_i] \qquad (13.60)$$

Except for a very few cases, the value of ΔS°_a is mainly determined by the number of atoms in a molecule of a compound. With comparatively great fluctuations in the values of ΔS°_a, we can narrow the interval of the fluctuations by combining substances according to the feature of the same type of molecule (with respect to compo-

sition and structure) into subgroups. Thus, for 42 studied pentatomic compounds, ΔS_a° varies within the limits from −127 to −183 e.u., for oxides and sulphides (Me_2O_3 and Me_2S_3) from −173 to −183 e.u., for $MeCO_3$ and $MeSiO_3$ from −164 to −175 e.u., for compounds of the type $MeXO_3$ (X = N, Cl, Br or I) from −157 to −163 e.u.

Within a subgroup of compounds of the same type, in turn, laws are discovered that are due to the kind of metal, acid residue and to the position of the relevant element in the periodic table. For example, a transition within one subgroup of the periodic table from an element with a smaller atomic weight to one with a greater weight is attended by lowering of the absolute values of ΔS_a° for compounds of the same type.

As a result, the law of changes in ΔS_a° manifests itself so clearly that unknown values of ΔS_a° can be predicted and used to compute the standard entropies of substances not yet studied with the aid of Eq. (13.58). The changes in entropy upon the transition of one gramme-atom of an element from its normal state in standard conditions to the state of an ideal monoatomic gas, i.e. the quantities $(S_{el}^\circ)_i - S_{el}^\circ$ needed for these calculations, are known for almost all elements; they are given in Table 20. Their calculation was based on the values of the standard entropy of the elements, the heats of dissociation and sublimation (or vaporization), and the saturated vapour pressure at 25 °C.

Table 20. **Change in Entropy upon the Transition of 1 g-atom of an Element from Its Normal State in Standard Conditions to the State of an Ideal Monoatomic Gas**

H	11.78	Hg	23.3	Zr	33.8	W	33.6
Li	26.45	B	35.0	Hf	31.6	F	13.64
Na	24.52	Al	32.56	N	13.72	Cl	12.81
K	23.1	Ga	30.19	P	28.4	Br	23.46
Rb	24.0	In	(29.2)	As	33.2	I	29.2
Cs	22.2	Tl	27.8	Sb	32.6	Mn	33.89
Cu	31.78	Sc	(33.8)	Bi	31.1	Fe	36.63
Ag	31.13	Y	(32.4)	V	36.6	Co	36.1
Au	31.74	La	29.9	Nb	(31.99)	Ni	36.4
Be	30.28	C	36.41	O	13.96	Ru	37.6
Mg	35.51	Si	35.63	S	32.48	Rh	36.8
Ca	27.05	Ge	30.0	Se	31.2	Pd	31.0
Sr	(26.7)	Sn	27.9	Te	31.8	Os	(38.0)
Ba	(24.5)	Pb	26.4	Cr	36.0	Ir	36.6
Zn	28.46	Ti	36.5	Mo	36.6	Pt	36.0
Cd	27.8						

It was thus possible to predict the unknown values of the standard entropies for many compounds with an accuracy from 0.3 to 1.5 e.u. (some of these data have been included in Table 18). The error of the calculations averages 1-2 e.u. and only in a few cases does it grow to 5 e.u. When the entropy is compared for a large number of compounds and with highly accurate data used to calculate ΔS°_a, the error of the calculations decreases to less than one entropy unit.

As a result of excluding the influence of the state of aggregation of elements, definite laws can be noted in the values of ΔS°_a. This is still more characteristic of ΔS°_i, because the influence of the state of aggregation of the compound itself is excluded in this quantity: the values of ΔS°_i within the groups fluctuate less, and there is a sharper boundary between the values of ΔS°_i for different groups than for ΔS°_a. For example for 52 studied biatomic compounds, ΔS°_a ranges from −52 to −74 e.u., whereas ΔS°_i ranges from −17 to −28 e.u.; for 15 halides MeHal, the former quantity ranges from −56 to −62, and the latter from −19.5 to −22.5, and so on. The insignificant fluctuations for similar compounds within a subgroup make it possible to predict the values of S° for compounds not studied with great accuracy.

The limited amount of experimental data [ΔH_{vap}, ΔH_{subl}, $p = \varphi(T)$] available for compounds, and also the impossibility of establishing these data in a number of cases for unstable compounds, for example for crystallohydrates, carbonates and double salts, do not make it possible to widely use calculations of ΔS°_i. Therefore, V. Kireev performed the calculations using ΔS°_a for 260 compounds, whereas calculations by means of ΔS°_i were successful for only 70 compounds.

A. Kapustinsky and K. Yatsimirsky (1948) proposed a method for calculating the entropy of crystalline compounds of the ionic type based on the additivity of the entropies of ions in a crystal. The value of $S^c_{K^+} = 10$ e.u., which corresponds to a value of $S^c_{KCl} = 19.8$ e.u., was taken as the initial value. The entropies of ions needed for the calculations can be found either from those of studied compounds on the basis of the additivity rule, or by the equation

$$S^c_i = \frac{3}{2} R \ln A - \frac{1.5z^2}{r} \qquad (13.61)$$

where A = atomic weight of an ion
z = charge of the ion
r = its radius in Å.

Checking for 30 compounds formed by ions with one or two charges showed that the discrepancies between the calculated and experi-

mental data do not exceed two entropy units. The additivity rule will hardly be observed for ions with a greater number of charges.

In developing his method for calculating entropy, Kireev showed that good results can be achieved in calculations by considering a reaction of formation of a compound not from simple substances, but from more complicated constituent parts, for example of metal carbonates from metal oxides and carbon dioxide, aqueous salts and $H_2O(c)$, etc. Here not only the influence of the difference in valence, but also to a considerable extent the difference in structure is excluded, since compounds of the same type are compared. Thus, for salts of oxygen acids of the same type, we have

$$S^\circ = \Sigma S^\circ_{\text{oxid}} + \Delta S^{\circ\prime}$$

where in a first approximation $\Delta S^{\circ\prime} = 0$, and in a second $\Delta S^{c\prime} = \text{const}$.

R. Wenner [C28] recommends the following approximate relationships:

for solid compounds

$$S = A \log M + B \tag{13.62}$$

for gases

$$S = A' M^{B'} \tag{13.63}$$

where M is the molecular weight.

The coefficients A, B, A' and B' in these equations are constant for substances of the same type. Consequently, having at our disposal the values of the entropies of two representatives of a group of compounds (for example of the halides MeHal or oxides MeO), we can find the entropies for the substances that have not been studied from a graph of $\ln S = \varphi(\ln M)$.

Such a procedure can also be used for calculations by Eq. (13.63), where A' and B' are constant for substances with an identical number of atoms in a molecule. The error in the calculations, as a rule, does not exceed 2-4 e.u. Let us consider two other equations in which the entropy of a substance is related to other properties.

According to E. Eastman (1923), the entropy of solids (calculated per gramme-atom) is

$$S = \frac{3}{2} R \ln A_{\text{av}} + R \ln V_{\text{av}} - \frac{3}{2} R \ln T_{\text{m}} + a \tag{13.64}$$

where A_{av} = average atomic weight, i.e. the molecular weight divided by the number of atoms in a molecule

V_{av} = average atomic volume, i.e. the average atomic weight divided by the density

a = constant equal to 12.5 ± 2 (for related substances the interval of fluctuations is smaller).

W. Hertz (1931) found that

$$S^\circ \sqrt[3]{c} \approx \text{const} = 4.9n \qquad (13.65)$$

where c = specific heat capacity at $t = 25\,^\circ\text{C}$
n = number of atoms in a compound.

Verification of Eq. (13.65) for the elements of halides (with molecules consisting of two, three or four atoms) and sulphides (two, three, four or five atoms per molecule) showed that the average error does not exceed one or two entropy units.

Among other equations, the approximate formula proposed by K. Yatsimirsky (1947) should be mentioned —

$$S = \Sigma S_{el} - a\Delta V \qquad (13.66)$$

whose accuracy for binary compounds was assessed by the author at ± 2 e.u. (all the values of V are taken for solid elements). This equation may be applied for more complicated compounds, and in these cases ΣS_{el} may be equated to the sum of the entropies of the constituent parts of a molecule (for example Na_2O and SiO_2 for Na_2SiO_3). Here ΔV will be the difference between the volume of one mole of the compound and the sum of the molar volumes of its constituent parts. When ΔV is expressed in cm^3/mol, the proportionality factor $a \approx \frac{1}{3}$.

A. Kapustinsky (1941) established that for solutions (1) the entropies of ions having identical dimensions are linear functions of the ion charges; and (2) the entropies of ions of an identical valence are a linear function of the reciprocals of the ion radii.

Example 18. Use the data given in Tables 18 and 20 and in Appendix 2 to find the entropy of formation of KCl from its elements taken in the state of a monoatomic ideal gas. On the basis of the value obtained, calculate S°_{298} for KHal and MeCl. Also assess the accuracy of calculations of S°_{298} according to Kireev's method for MeHal.

Solution. In accordance with the tabulated data, the entropies of the elements in the idealized state are

$$(S_i)_K = 23.1 + 15.34 = 38.44 \text{ e.u.}$$

$$(S_i)_{Cl} = 12.81 + 0.5 \times 53.293 = 39.46 \text{ e.u.}$$

Hence by Eq. (13.58)

$$(\Delta S^\circ_a)_{KCl} = 19.73 - (38.44 + 39.46) = -58.17 \text{ e.u.}$$

Assuming that the found value also equals ΔS°_a for KBr, we get

$$-58.17 = (S^\circ_{KBr})_{298} - [38.44 + (23.46 + 0.5 \times 36.38)]$$

whence $(S^\circ_{KBr})_{298} = 21.92$ e.u., which differs from the tabulated

value by 1.0 e.u. The average discrepancy for studied salts of the type KHal is about 1.2 e.u.

Calculations of S°_{298} for NaCl, RbCl, CuCl, AgCl, HgCl and TlCl (a common anion) give results differing from calorimetric data by an average of 0.8 e.u. The average discrepancy for 19 studied compounds of the type MeHal is 1.2 e.u.

Example 19. Use Kapustinsky's and Yatsimirsky's method to calculate the standard entropy of NaI if $r_{Na^+} = 0.95$ and $r_{I^-} = 2.16$ Å.

Solution. 1. Applying the additivity rule, on the basis of the data given in Table 18 and Appendix 2 we find

$$S^c_{I^-} = S^\circ_{KI} - S^c_{K^+} = 24.9 - 10 = 14.9 \text{ e.u.}$$

$$S^c_{Cl^-} = S^\circ_{KCl} - S^c_{K^+} = 19.8 - 10 = 9.8 \text{ e.u.}$$

$$S^c_{Na^+} = S^\circ_{NaCl} - S^c_{Cl^-} = 17.2 - 9.8 = 7.4 \text{ e.u.}$$

Hence

$$S^\circ_{NaI} = S^c_{Na^+} + S^c_{I^-} = 7.4 + 14.9 = 22.3 \text{ e.u.}$$

which differs from the tabulated value by about 1.7 e.u.

2. By Eq. (13.61) we get

$$S^c_{Na^+} = \frac{3}{2} R \ln 23.0 - 1.5 \times \frac{1^2}{0.95} = 7.77 \text{ e.u.}$$

$$S^c_{I^-} = \frac{3}{2} R \ln 126.9 - 1.5 \times \frac{1^2}{2.16} = 13.75 \text{ e.u.}$$

whence $S^\circ_{NaI} = 7.77 + 13.75 = 21.52$ e.u.

Example 20. Calculate the standard entropy of KCl by Eqs. (13.62), (13.64) and (13.65) and compare the results with the precise value of $S^\circ_{298} = 19.73$ e.u.

Solution. 1. For calculations by Eq. (13.62), we use the values of $S^\circ_{NaCl} = 17.34$ and $S^\circ_{KBr} = 23.05$ e.u. After substitution, we get

$$17.34 = 1.7668A + B \text{ and } 23.05 = 2.0756A + B$$

whence $A = 18.6$ and $B = -15.6$. Therefore, for halides we have

$$S^\circ_{MeHal} = 18.6 \log M - 15.6$$

whence $S^\circ_{KCl} = 19.2$ e.u.

2. From a reference book we find $\rho_{KCl} = 1.992$ g/cm³ ([D4], **5**: 183) and $(t_m)_{KCl} = 772.3$ °C ([D4], **7**: 323). By Eq. (13.64) we get

$$S^\circ_{KCl} = 4.576 \left(\frac{3}{2} \log \frac{74.553}{2} + \log \frac{74.553}{2 \times 1.992} - \frac{3}{2} \log 1045.5 \right) + 12.5 = 8.3 \text{ cal/K·g-atom}$$

whence $S^\circ_{KCl} = 16.6$ e.u.

3. By Eq. (13.65)

$$S^\circ_{KCl} = \frac{4.9 \times 2}{\sqrt[3]{0.164}} = 17.5 \text{ e.u.}$$

where 0.164 is the specific heat capacity of KCl at $t = 25\,°C$ (see Appendix 2).

Organic Substances. To assess S for organic compounds in the state of an ideal gas, we can use a method similar to that of calculating the standard heat of formation [C10] (see p. 54ff). The necessary quantities are given in Appendix 3. The discrepancy from experimental data does not exceed 2 e.u. Equation (13.62) can be recommended for approximate calculations.

Data obtained by comparing the change in the values of ΔS due to different changes in the molecular structure can be used for a very approximate assessment of the entropy of compounds in the solid and liquid states. A summary of such data is given in Table 21.

The equations proposed by I. Strelkov (1936) can also be used for an approximate assessment:

$$S^c \approx 1.1 C_p^c \quad \text{and} \quad S^{lq} \approx 1.4 C_p^{lq} \tag{13.67}$$

The standard entropies of liquid aliphatic hydrocarbons with a branched chain and of aromatic hydrocarbons can be assessed by the equation

$$S \approx 25.0 + 7.7m + 4.5r + 19.5p_1 + 26.5p_2 \tag{13.68}$$

where m = total number of carbon atoms outside a ring
r = number of branches
p_1 = number of phenyl groups
p_2 = number of saturated rings (of cyclopentane or cyclohexane).

Example 21. Calculate the standard entropy of gaseous 2,3-dimethylhexane and 2,2-dimethylhexane.

Solution. For 2,3-dimethylhexane, we have (Appendix 3)

	(A)	(B)	
Basic substance (CH_4) (Appendix 3A)			44.50
Substitution of primary H by CH_3 group (Appendix 3B)			10.35
Substitution of secondary H by CH_3 group (Appendix 3C)	1	1	10.10
	1	2	9.18
	1	2	9.18
	1	2	9.18
Side methyl groups (Appendix 3C)	2	2	7.15
	2	3	6.53
			106.17 e.u.

Table 21. **Changes in S°_{298} Depending on Changes in Molecular Structure [B79]**

Change in structure	Change in molar entropy of	
	crystalline substance	liquid
Introduction of group $-C\begin{matrix}O\\O\end{matrix}$ into hydrocarbon chain in the formation of an ester	—	13.2
Introduction of bond —O— into chain in the formation of an ether	—	5.0
Substitution of H in main hydrocarbon chain by CH_3 group	5.0 (?)	3.2
Substitution of H in main hydrocarbon chain by C_2H_5 group	—	10.9
Substitution of H by CH_3 group in hydrocarbon ring	5.8	7.7
Substitution of H by C_2H_5 group in hydrocarbon ring	11.6 (?)	15.4
Substitution of H by COOH group with the formation of an acid	5.8	7.7
Substitution of H by NH_2 group with the formation of an amine	0.0	0.0
Substitution of H by NO_2 group with the formation of a nitrocompound	7.0	8.0
Substitution of H by OH group with the formation of a primary monoatomic alcohol	0 (?)	—1.5
Substitution of H by OH group with the formation of a secondary monoatomic alcohol	0.5 (?)	—4.0
Substitution of H by OH group with the formation of a tertiary monoatomic alcohol	0.5 (?)	—6.0
Substitution of H by OH group with the formation of a phenol	0.0	0 (?)
Substitution of H by OH group with the formation of a polyhydroxylated compound	0.5 (?)	0.5 (?)
Substitution of H by bromine	7.5	9.0 (?)
Substitution of H by iodine	9.0 (?)	11.0 (?)
Substitution of H by chlorine	6.0	7.0 (?)
Substitution of H by C_6H_5 group bound to C	17.0	19.5
Substitution of H bound to C by cyclohexane or cyclopentane ring	—	26.5

Table 21 (concluded)

Change in structure	Change in molar entropy of	
	crystalline substance	liquid
Substitution of 2H by oxygen in the formation of an aldehyde	1.0 (?)	5.0 (?)
Substitution of 2H by oxygen in the formation of a ketone	1.0	0.5 (?)
Substitution of O by bivalent sulphur	2.0 (?)	2.0 (?)
Transformation of a single bond to a double one of the ethene type	−2.7	−2.7
Extension of a hydrocarbon chain by the group CH_2	5.8	7.7

which differs from the experimental value of 106.11 by 0.06 e.u.

For 2,2-dimethylhexane, the components of S°_{298} are the same except for the last value, which equals 3.87 [(A) = 3 and (B) = 2]. Therefore for this compound, $S^\circ_{298} = 103.51$ e.u., which differs from the experimental value of 103.06 by 0.45 e.u.

Comparative Calculations. For approximate calculations of the entropy of inorganic and organic compounds, methods of comparative calculations [B45] can be used, particularly the relationships

$$S_{II} \approx AS_I + B \tag{13.69}$$

$$S \approx AY + B \tag{13.70}$$

which correspond to a comparison (in given conditions) of the values of S in two series I and II of similar substances (an example of the first method of comparative calculations), and of the values of S and the characteristic Y in one series of similar substances (an example of the second method of comparative calculations), and also a relationship of the kind

$$S_N \approx AS_M + B \tag{13.71}$$

where the values of S for two substances (M and N) are compared at identical values of a variable parameter (an example of the fourth method of comparative calculations). Expression (13.69) is illustrated by the relationship shown in Fig. 175. The linear relationship is a result of the similarity in slope for the values of S°_{298} in the series of similar substances being compared (see Fig. 173); in each

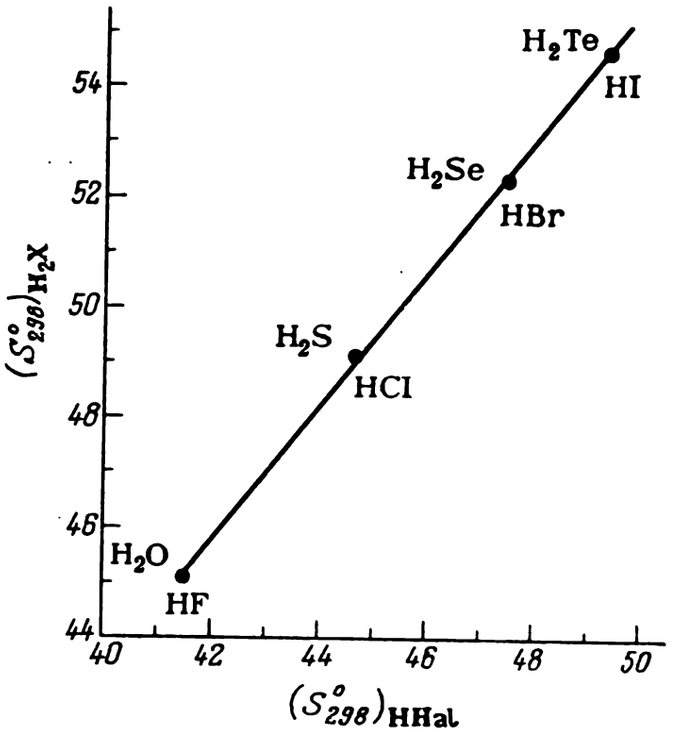


Fig. 175. Relationship between the standard entropies of compounds of the same type HHal (Hal = F, Cl, Br or I) and H_2X (X = O, S, Se or Te)

series the molecules contain a common particle and differ in particles that are analogues according to the periodic table of the elements. The closer the series being compared, the nearer is A in expression (13.69) to unity. This can be seen directly from Fig. 176.

Another example of expression (13.69) is the relationship

$$(S^\circ_{298})_{el.hyd(g)} \approx (S^\circ_{298})_{el.fl(g)} - 7.3$$

(with an average error less than 0.3 e.u.) between the standard entropy of gaseous hydrides and that of fluorides of alkali metals which indicated the above analogy between hydrogen and the halogens. For the most closely related substances, we have not only $A_1 \approx 1$, but also $B_1 \approx 0$ (straight line I in Fig. 176).

An example of expression (13.70) is the relationship shown in Fig. 177 — a growth in the density of the isostructural analogues (rutile-like modifications of SiO_2) diminishes their entropy. Another example is the linear relationship between the entropy and heat capacity ($Y = C_p$) in certain series of similar compounds.

Figure 178 shows the validity of expression (13.71) using as an example different pairs of similar substances. Notice should be taken of straight line III: first, the similarity between CO and N_2 is so great that $A_1 \approx 1$ for them; second, the similarity extends throughout the entire studied interval of temperatures covering teh gaseous, liquid and solid states of these substances-analogues.

Expression (13.71) can also be used in the form of the relationship

$$(S_T^\circ - S_{298}^\circ)_N \approx A(S_T^\circ - S_{298}^\circ)_M + B$$

Here also we often have $A \approx 1$ (or $B \approx 0$).

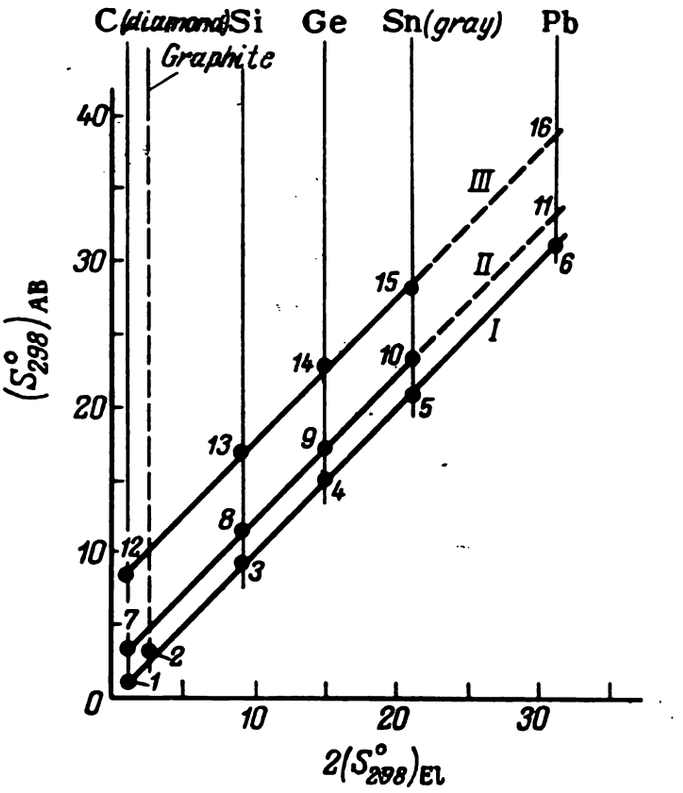


Fig. 176. Relationship between double standard entropies S_{298}° of elements of the carbon subgroup and standard entropies of the compounds $A^{III}B^{V}$ (*I*), $A^{II}B^{VI}$ (*II*) and $A^{I}B^{VII}$ (*III*):
1—BN (borazone); *2*—BN; *3*—AlP; *4*—GaAs; *5*—InSb; *6*—TlBi; *7*—BeO; *8*—MgS; *9*—CaSe; *10*—SrTe; *11*—BaPo; *12*—LiF; *13*—NaCl; *14*—KBr; *15*—RbI; *16*—CsAt

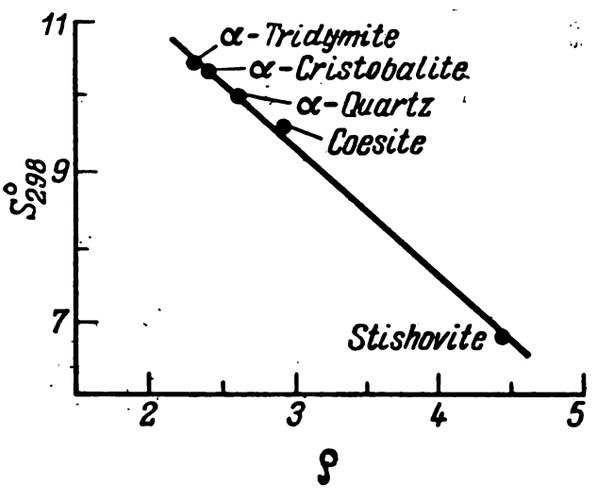


Fig. 177. Standard entropy against density for different modifications of SiO_2

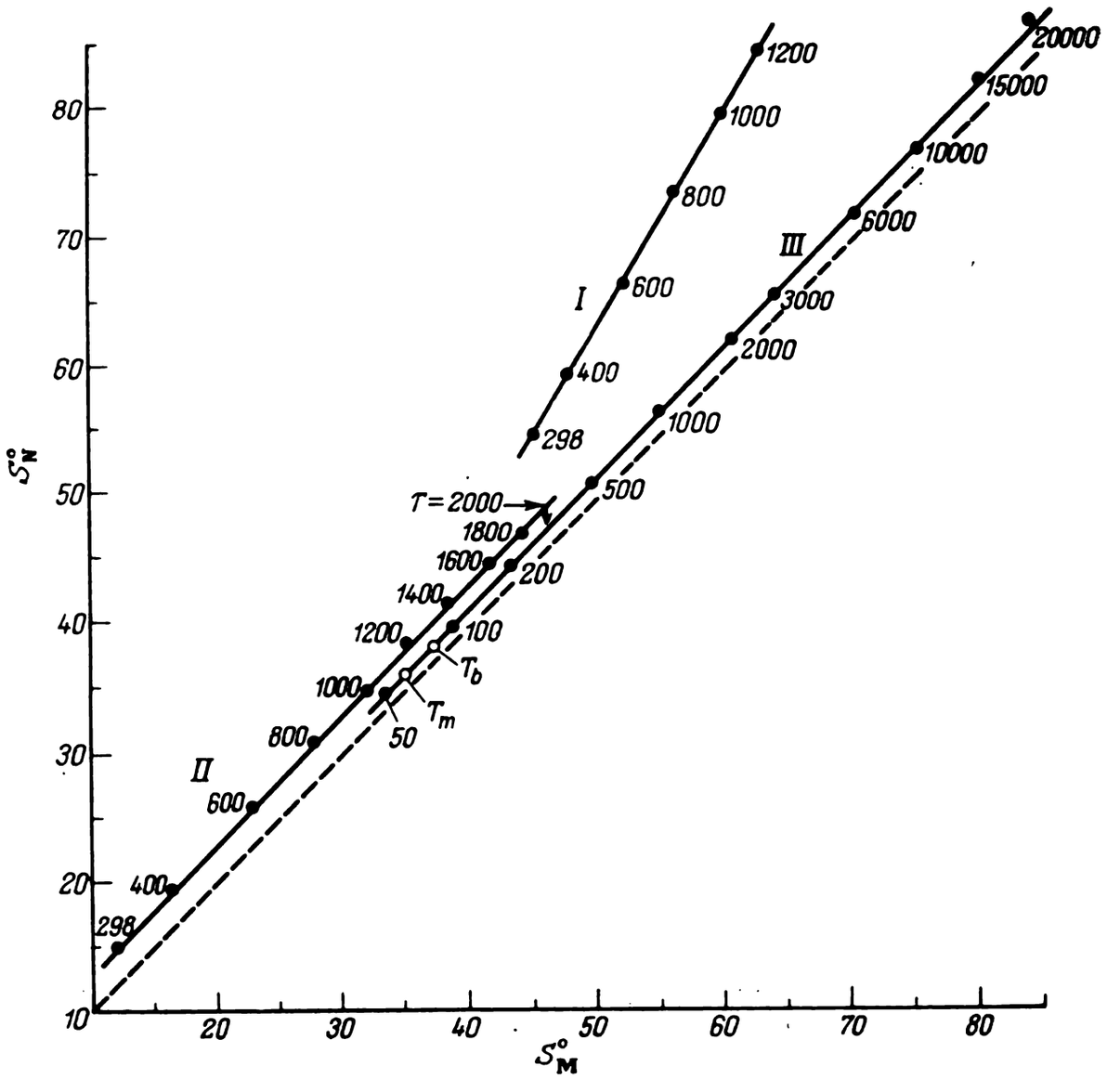


Fig. 178. Relationship between standard entropies of similar substances at the same temperature:
I—CH_4 (M) and C_2H_6 (N); *II*—ZrO_2 and HfO_2; *III*—N_2 and CO

13.7.2. Calculating Equilibrium

Equilibrium is calculated on the basis of Eq. (5.22)

$$\Delta G^\circ_T = \Delta H^\circ_T - T\Delta S^\circ_T \qquad (13.72)$$

where ΔS°_T is the algebraic sum (taking into account the stoichiometric coefficients) of the standard entropies S°_T of the reagents.

After computing ΔG°_T, Eq. (13.8) is used to find the equilibrium constant for a given temperature, and Eqs. (13.20) and (13.21) to find ΔG° and K_a for any temperature. Thus the problem of calculating equilibrium using only *thermal* data has been solved. When values of S°_{298} are available (see pp. 484ff), the calculations are simplified even more, because in this case the equation used for calculations becomes

$$\Delta G^\circ_{298} = \Delta H^\circ_{298} - 298.2\Delta S^\circ_{298} \qquad (13.73)$$

i.e. it is no longer necessary to calculate the entropies of the reagents and their heat effects, since the values of ΔH°_{298} can be taken from tables or determined indirectly (for instance according to Hess's law). It should be noted in passing that it was precisely Eq. (13.73) which was used to calculate the values of ΔG°_{298} for many compounds.

When tabulated values of $H^\circ_T - H^\circ_{298}$ and $S^\circ_T - S^\circ_{298}$ are available for all the reagents, we can use the equation

$$\Delta G^\circ_T = \Delta H^\circ_{298} - T\Delta S^\circ_{298} + \Delta(H^\circ_T - H^\circ_{298}) - T\Delta(S^\circ_T - S^\circ_{298})$$

The heat effect of a reaction can also be found similarly to ΔS°_T by algebraic summation of the enthalpies of the relevant substances. By combining Eqs. (13.8) and (13.56), we get

$$\log K_a = \frac{1}{4.576}\left(\Delta S^\circ_T - \frac{\Delta H^\circ}{T}\right)$$

or

$$\log K_a = \frac{1}{4.576}\left[\Delta S^\circ_T - \frac{\Delta(H^\circ_T - H^\circ_0)}{T} - \frac{\Delta H^\circ_0}{T}\right] \qquad (13.74)$$

In this equation, the enthalpy of each reagent is counted from absolute zero $(H^\circ_T - H^\circ_0)$ and is determined by the equation

$$H^\circ_T - H^\circ_0 = \sum \int C_p\, dT + \sum \Delta H_{\text{ph.tr}} \qquad (13.75)$$

while the hypothetical heat effect at absolute zero is determined by the equation

$$\Delta H^\circ_0 = \Delta H^\circ_T - \Delta(H^\circ_T - H^\circ_0) \qquad (13.76)$$

The following equation can be used to calculate ΔH°_T for the basic temperature T (see p. 79) :

$$\Delta H^\circ_{T_1} = -T\left\{R \ln K_T + \Delta\left[\frac{(G^\circ_T - H^\circ_{T_1})}{T}\right]\right\} \qquad (13.77)$$

Calculations of equilibrium on the basis of absolute values of the entropies allow us to check how far experimental data coincide with calculated figures. Such verification for pure crystalline substances have confirmed the validity of the third law of thermodynamics.

For reactions involving organic substances, the discrepancies between the values of ΔS°_T calculated according to the third law on the basis of Eq. (13.54) and those found by means of the heat effects and equilibrium constants or by means of the e.m.f. by the equation

$$\Delta S^\circ_T = 23\,062n\frac{\partial E^\circ}{\partial T} \qquad (13.78)$$

obtained from Eqs. (13.2) and (13.56) also do not generally deviate beyond the limits of experimental errors (Table 22).

Table 22. **Comparison of Values of ΔS°_{298} for Selected Reactions Found from Equilibrium and Thermochemical Data**

Reaction	ΔS°_{298} by Eq. (13.72) or (13.78)	ΔS°_{298} by Eqs. (13.54) and (13.56)
$Ag + \frac{1}{2} Br_2(lq) = AgBr$*	−3.02	−2.95
$Ag + \frac{1}{2} Cl_2(g) = AgCl$	−13.73	−13.86
$Ag + \frac{1}{2} Hg_2Cl_2 = AgCl + Hg$	−7.78	−7.54
$C + 2H_2 = CH_4$	19.4	19.8
$C + \frac{1}{2} O_2 = CO$	21.14	21.34
$(CH_3)_2CHOH(lq) = (CH_3)_2CO(lq) + H_2$	36.4	36.1
$CO + H_2O(lq) = HCOOH(lq)$	−30.3	−30.1
$HOOC(CH_2)_2COOH(c) = trans\text{-}COOHCH{=}CHCOOH(c) + H_2$	30.0	28.9
$C_6H_4(OH)_2(c) = C_6H_4O_2(c) + H_2$**	35.5	36.4
$CaCO_3 = CaO + CO_2$	38.10	38.37
$H_2 + O_2 + C = HCOOH(lq)$	−49.3	−50.75
$2H_2 + \frac{1}{2} O_2 + N_2 + C = CO(NH_2)_2(c)$	−108.2	−108.9
$Mg(OH)_2 = MgO + H_2O(g)$	36.67	36.45
$\frac{1}{2} Pb + AgCl = \frac{1}{2} PbCl_2 + Ag$	4.29	4.50
$\frac{1}{2} Pb + AgI = \frac{1}{2} PbI_2 + Ag$	3.99	4.23
S(rhomb.) = S(monocl.)	−0.22	−0.15
Sn (gray) = Sn (white)	1.87	1.75
$Zn + \frac{1}{2} O_2 = ZnO$	−24.24	−24.02

* $T = 265.9$ K.
** $T = 285$ K.

We can thus state that the third law holds equally for reactions of both inorganic and organic substances. This makes it possible to use it very widely in organic chemistry, where there are often no other ways of solving the problem, because reactions quite frequently proceed too slowly for direct measurement of equilibrium.

It should be noted that the low accuracy of the values of the heat effects limits the authenticity of the results of calculating equilibrium. Errors in determining the heat effects have a much greater influence on the results of calculations than inaccuracies in calculating the entropy. Even an error as big as ± 3 entropy units results in an error in the value of ΔG°_{298} less than ± 900 cal, which in the majority of cases is less than the possible error in ΔH°. Because ΔH° is responsible for the greater part of the error in the equilibrium constant, the validity of the third law was doubted for a long time.

It must be stressed that the *absolute* error in determining the entropy, and not its relative value, is important for calculating equilibrium.

Example 22. Use the data given in Fig. 163 for the reaction

$$C_2H_4 + H_2O(g) = C_2H_5OH(g)$$

and in Tables 1, 9, 10 and 18 and in Appendix 9 to calculate the standard entropy of ethene.

Solution. For the above process in accordance with Fig. 165

$$\log K_p \approx \frac{2280}{T} - 6.45 \quad \text{and} \quad \log (K_p)_{298} = 1.20$$

whence

$$\Delta G^\circ_{298} = -4.576 \times 298.2 \times 1.20 = -1637 \text{ cal/mol}$$

For the reaction of preparing liquid ethanol from ethene, according to the data of Table 1, we have

$$\Delta H^\circ_{298} = -66\,190 - [12\,540 + (-57\,796)] = -20\,934 \text{ cal/mol}$$

The heat of vaporization of ethanol at $t = 25\,^\circ\text{C}$ in accordance with Eq. (7.35) and the data of Appendix 9 and Table 10 is approximately $1.13 \times 8970 = 10\,133$ cal/mol. Consequently, for the synthesis of gaseous ethanol $\Delta H^\circ_{298} = -10\,798$ cal/mol. By Eq. (13.71)

$$\Delta S^\circ_{298} = \frac{-10\,798 - (-1637)}{298.2} = -30.72 \text{ cal/mol} \cdot \text{K}$$

and from Table 18

$$(S^\circ_{\text{ethene}})_{298} = 67.5 - 45.106 - (-30.72) = 53.11 \text{ cal/mol} \cdot \text{K}$$

The coincidence of the found value with the tabulated one is good, although the probable error of ΔG°_{298} may reach 10-30%.

Example 23. Show that ΔS° can be determined on the basis of the values of K and the relationship $K = \varphi(T)$.

Solution. In accordance with the equation $(\partial \Delta G/\partial T)_p = -\Delta S$ written down for standard conditions and Eq. (13.8), we get

$$\Delta S^\circ = R\left(T\frac{d\ln K}{dT} + \ln K\right)$$

or for a comparatively narrow interval of temperatures

$$\Delta \bar{S}^\circ_T \approx 4.576\left(T_{av}\frac{\log K_{T_2} - \log K_{T_1}}{T_2 - T_1} + \frac{\log K_{T_2} + \log K_{T_1}}{2}\right)$$

13.7.3. Approximate Methods of Calculating Equilibrium According to Standard Data

Since

$$\Delta H^\circ_T = \Delta H^\circ_{298} + \int_{298}^{T} \Delta C_p\, dT \quad \text{and} \quad \Delta S^\circ_T = \Delta S^\circ_{298} + \int_{298}^{T} \frac{\Delta C_p}{T}\, dT$$

then by Eq. (5.22)

$$\Delta G^\circ_T = \Delta H^\circ_{298} - T\Delta S^\circ_{298} - T\int_{298}^{T}\frac{\Delta C_p}{T}\,dT + \int_{298}^{T}\Delta C_p\,dT =$$

$$= \Delta H^\circ_{298} - T\Delta S^\circ_{298} - T\int_{298}^{T}\frac{dT}{T^2}\int_{298}^{T}\Delta C_p\,dT \qquad (13.79)$$

We shall consider conditionally that $\Delta C_p = \text{const} = a$. Therefore Eq. (13.79) will become

$$\Delta G^\circ_T = \Delta H^\circ_{298} - T\Delta S^\circ_{298} - aTM_0 \qquad (13.80)$$

where

$$M_0 = \ln\frac{T}{298.2} - 1 + \frac{298.2}{T}$$

(the values of M_0 are given in Table 23).

When the temperature dependence of C_p is known for all the reagents within a broad range of temperatures, calculations by Eq. (13.79) involve no difficulties, because the values of ΔS°_{298} and ΔH°_{298} can be found with the aid of the relevant tables. This method of calculations, however, is not suitable for reactions between substances which proceed at very high temperatures or between substances which have been inadequately studied. In these cases, the following approximate methods of calculation can be recommended.

First Approximation. Assume that $a = \Delta C_p = 0$. Hence Eq. (13.80) becomes

$$\Delta G_T^\circ = \Delta H_{298}^\circ - T\Delta S_{298}^\circ \qquad (13.81)$$

therefore

$$\log K_p = -\frac{\Delta H_{298}^\circ}{4.576T} + \frac{\Delta S_{298}^\circ}{4.576} \qquad (13.82)$$

The latter equation is identical with Eq. (13.11) on the condition that $\Delta S_{298}^\circ = 4.576B$, and with Eq. (13.44) on the condition that $\Delta n = 0$ and $\Delta S_{298}^\circ = -4.576\Delta i$.

The first approximation gives satisfactory results for many important reactions in practice (at any rate for most reactions up to 500-600 K) and can be employed when calculating the equilibrium constants in the absence of accurate experimental data. * A merit of this method is the availability of the values of ΔH_{298}° and S_{298}°.

Second Approximation. Let us take into account the change in ΔH° and ΔS° with a change in temperature, assuming that $a = (\Delta C_p)_{298} = \text{const}$. Hence Eq. (13.80) becomes

$$\Delta G_T^\circ = \Delta H_{298}^\circ - T\Delta S_{298}^\circ - (\Delta C_p)_{298} TM_0 \qquad (13.83)$$

therefore

$$\log K_p = -\frac{\Delta H_{298}^\circ}{4.576T} + \frac{\Delta S_{298}^\circ}{4.576} + \frac{(\Delta C_p)_{298}}{4.576} M_0 \qquad (13.84)$$

When ΔC_p changes greatly with a change in temperature, the second approximation may give poorer results than the first. In this case, it is recommended to use the mean values of the heat capacities (between 298.2 and T K).

It pays to go over from the first to the second approximation only when the quantity $(\Delta C_p)_{298} TM_0$ is greater than the errors in ΔH_{298}° and $T\Delta S_{298}^\circ$ for a given reaction. The greater these errors, the higher should be the values of $(\Delta C_p)_{298}$. For instance, if $T \leqslant 1000$ K, while the errors in ΔH_{298}° and ΔS_{298}° do not exceed ± 10 and ± 0.05 cal/mol, respectively, the second approximation should always be used, and whenever possible, a still more accurate equation (see below); if these errors equal ± 1000 and ± 5 cal/mol, the second approximation should be used only when $(\Delta C_p)_{298} > 10$.

Since $\Delta S > \Delta C_p$, the Gibbs energy of a reaction depends much more considerably on the temperature than its heat effect.

The relationship between the temperature coefficients of the quantities ΔG° and ΔH° can be assessed according to the results

* The value of ΔC_p is usually not great for reactions in the gaseous phase. In addition, mutual compensation in the changes in ΔH_{298}° and ΔS_{298}° with the temperature has an effect, because $(\partial \Delta H/\partial T)_p = \Delta C_p$, while $(\partial \Delta S/\partial T)_p = \Delta C_p/T$.

of calculations for selected reactions given below:

	$\frac{\Delta H^\circ_{1500} - \Delta H^\circ_{300}}{1200}$	$\frac{\Delta G^\circ_{1500} - \Delta G^\circ_{300}}{1200}$
$C + CO_2 = 2CO$	1.47	42.2
$C + H_2O(g) = CO + H_2$	1.04	34.1
$CO + \frac{1}{2} O_2 = CO_2$	0.52	20.9
$CO + H_2O(g) = CO_2 + H_2$	2.20	8.25
$CH_4 + \frac{1}{2} O_2 = CO + 2H_2$	2.53	46.2
$CH_4 + CO_2 = 2CO + 2H_2$	2.01	67.1
$CH_4 + H_2O(g) = CO + 3H_2$	4.21	59.1
$CH_4 + 2H_2O(g) = CO_2 + 4H_2$	6.42	50.9

When the mean heat capacities are known for the interval $T_1 - T$, the following approximate equation can be used for calculations:

$$\Delta G^\circ_T = \Delta H^\circ_{T_1} - \Delta S^\circ_{T_1} + \Delta \bar{C}_p \left[(T - T_1) - T \ln \frac{T}{T_1} \right]$$

For reactions in solutions, however, it may give erroneous results even within a small temperature interval (50 to 100 K).

Third Approximation. It is assumed that $a = \Delta C_p = \varphi(T)$. The entire temperature interval for which equilibrium is being calculated is divided into portions, and a single (constant) value of a is selected for each. Thus, H. Ulich recommends the selection of these portions proportional to log T, for example 300-600, 600-1200, 1200-2400 K for which the mean values of C_p are determined:

$$\left.\begin{aligned} (\Delta \bar{C}_p)_{300-600} &= \frac{1}{2} [(\Delta C_p)_{300} + (\Delta C_p)_{600}] \\ (\Delta \bar{C}_p)_{600-1200} &= \frac{1}{2} [(\Delta C_p)_{600} + (\Delta C_p)_{1200}] \\ (\Delta \bar{C}_p)_{1200-2400} &= \frac{1}{2} [(\Delta C_p)_{1200} + (\Delta C_p)_{2400}] \end{aligned}\right\} \qquad (13.85)$$

Next a second set of mean values $(\Delta\bar{\bar{C}}_p)$ is determined. The most accurate results are obtained if we assume that for

$$
\left.\begin{aligned}
&(1)\ T = 300\text{-}450, && a_1 = (\Delta\bar{\bar{C}}_p)_1 = (\Delta C_p)_{300}\\
&(2)\ T = 450\text{-}550, && a_2 = (\Delta\bar{\bar{C}}_p)_2 = \tfrac{1}{2}\,[(\Delta\bar{\bar{C}}_p)_1 + (\Delta\bar{\bar{C}}_p)_3]\\
&(3)\ T = 550\text{-}1100, && a_3 = (\Delta\bar{\bar{C}}_p)_3 = (\Delta\bar{C}_p)_{300\text{-}600}\\
&(4)\ T = 1100\text{-}1500, && a_4 = (\Delta\bar{\bar{C}}_p)_4 = \tfrac{1}{2}\,[(\Delta\bar{\bar{C}}_p)_3 + (\Delta\bar{\bar{C}}_p)_5]\\
&(5)\ T = 1500\text{-}2600, && a_5 = (\Delta\bar{\bar{C}}_p)_5 = \tfrac{1}{2}\,[(\Delta\bar{C}_p)_{300\text{-}600} + \\
& && \qquad + (\Delta\bar{C}_p)_{600\text{-}1200}]\\
&(6)\ T = 2600\text{-}3400, && a_6 = (\Delta\bar{\bar{C}}_p)_6 = \tfrac{1}{2}\,[(\Delta\bar{\bar{C}}_p)_5 + (\Delta\bar{\bar{C}}_p)_7]\\
&(7)\ T > 3400 && a_7 = (\Delta\bar{\bar{C}}_p)_7 = \tfrac{1}{2}\,[(\Delta\bar{C}_p)_{300\text{-}600} + \\
& && \qquad + (\Delta\bar{C}_p)_{600\text{-}1200} + (\Delta\bar{C}_p)_{1200\text{-}2400}]
\end{aligned}\right\} \quad (13.86)
$$

Unlike the calculations of equilibrium with the aid of power series for $\Delta C_p = \varphi(T)$ (see below), the present method always includes the possibility of changing and simplifying the calculations (depending on the required degree of accuracy); but for the usual accuracy of the values of ΔH and ΔS, it is generally not expedient to use the second and especially the third approximations.

The Temkin-Shwartsman Method. When accurate calculations are needed, it is better to use the method proposed by M. Temkin and L. Shwartsman (1948) instead of the complicated method of finding the mean values of a for each temperature interval (the third approximation). Let us write down Eq. (13.79) in the form

$$\Delta G^\circ_T = \Delta H^\circ_{298} - T\Delta S^\circ_{298} - T(M_0\Delta a + M_1\Delta b + M_2\Delta c + M_{-2}\Delta c') \quad (13.87)$$

In this equation, the value of M_0 coincides with M_0 in Eq. (13.80), while the functions of temperature M_1, M_2 and M_{-2} are expressed by the equation

$$M_n = \frac{T^n}{n(n+1)} + \frac{298.2^{n+1}}{(n+1)T} - \frac{298.2^n}{n} \quad (13.88)$$

The convenience of using Eq. (13.87) is due to the possibility of calculating the values of M_0, M_1, M_2 and M_{-2} beforehand for various temperatures (Table 23). It should be noted that this equation not only allows us to easily find the relationship $\Delta G^\circ = \varphi(T)$, but also to determine ΔH°_{298} and ΔS°_{298} when a number of values of ΔG° (or K_a) are available for different temperatures. For this purpose, a graph should be constructed by plotting $1/T$ along the axis of abscissas and $(\Delta G^\circ/T) + M_0\Delta a + \ldots$ along the axis of ordinates. Hence in accordance with Eq. (13.87), the slope of the straight line will determine ΔH°_{298}, and the ordinate intercept, the value of ΔS°_{298}. Thus, if the problem is to find the values of ΔH°_{298} and ΔG°_{298}, the method just treated should be considered the best, and not the method of simultaneously determining ΔH°_0 and I (the sigma-function method) treated in Sec. 13.4.2.

When $a = \Delta C_p = 0$, Eq. (13.87) coincides with Eq. (13.81), and when $a = \Delta C_p = \Delta a$, with Eq. (13.83).

Example 24. Using an approximate method of calculating equilibrium, find ΔG° at $T = 700$, 1100 and 1500 K for the reaction

$$CH_4 + H_2O(g) = CO + 3H_2$$

and compare the results of the calculations with the accurate values and with the data obtained in solving Example 7, p. 451.

Solution. From Table 1 for the reaction being considered, we have $\Delta H^\circ_{298} = 49\,260$ cal/mol, and from Appendix 2 we have $\Delta S^\circ_{298} = 51.16$ e.u. Hence by Eq. (13.81) (first approximation), we get

$$\Delta G^\circ = 49\,260 - 51.16T$$

Second approximation: $(\Delta C_p)_{298} \approx 11.10$ cal/mol · K (see Example 7), and by Eq. (13.80) we obtain

$$\Delta G^\circ = 49\,260 - 51.16T - 11.10TM_0$$

Third approximation: in accordance with the equation $\Delta C_p = \varphi(T)$ (Example 7) we get $(\Delta C_p)_{300} = 11.225$, $(\Delta C_p)_{600} = 7.031$ and $(\Delta C_p)_{1200} = 0.892$ cal/mol · K.

Using the found values of $(\Delta C_p)_T$, by Eq. (13.85) we calculate the mean values $\Delta\bar{C}_p$, namely, $(\Delta\bar{C}_p)_{300-600} = 9.128$ and $(\Delta\bar{C}_p)_{600-1200} = 3.962$ cal/mol · K. Next by Eq. (13.86) we consecutively find $a_1 = (\Delta\bar{\bar{C}}_p)_1 = 11.225$, $a_3 = (\Delta\bar{\bar{C}}_p)_3 = 9.128$, $a_2 = (\Delta\bar{\bar{C}}_p)_2 = 10.176$, $a_5 = (\Delta\bar{\bar{C}}_p)_5 = 6.545$ and $a_4 = (\Delta\bar{\bar{C}}_p)_4 = 7.837$.

Introducing into Eq. (13.80) the values of a_i, we calculate $\Delta G^\circ = \varphi(T)$. To increase the accuracy of the results, we take the average

Table 23. **Constants of Eqs. (13.80) and (13.87)**

T	M_0*	M_1** $\times 10^{-3}$	M_2*** $\times 10^{-6}$	M_{-2}**** $\times 10^{5}$
300	0.000	0.0000	0.0000	0.0000
400	0.0392	0.0130	0.0043	0.0364
500	0.1133	0.0407	0.0149	0.0916
600	0.1962	0.0759	0.0303	0.1423
700	0.2794	0.1153	0.0498	0.1853
800	0.3597	0.1574	0.0733	0.2213
900	0.4361	0.2012	0.1004	0.2521
1000	0.5088	0.2463	0.1134	0.2783
1100	0.5765	0.2922	0.1652	0.2988
1200	0.6410	0.3389	0.2029	0.3176
1300	0.7019	0.3860	0.2440	0.3340
1400	0.7595	0.4336	0.2886	0.34835
1500	0.8141	0.4814	0.3362	0.3610
1600	0.8665	0.5296	0.3877	0.3723
1700	0.9162	0.5780	0.4424	0.3824
1800	0.9635	0.6265	0.5005	0.3915
1900	1.009	0.6752	0.5619	0.3998
2000	1.0525	0.7240	0.6265	0.4072
2100	1.094	0.7730	0.6948	0.4140
2200	1.134	0.8220	0.7662	0.4203
2300	1.173	0.8711	0.8411	0.4260
2400	1.210	0.9203	0,9192	0.4314
2500	1.246	0.9696	1.0008	0.4363
2600	1.280	1.0189	1.0856	0.4408
2700	1.314	1.0683	1.1738	0.44505
2800	1.346	1.1177	1.2654	0.4490
2900	1.3775	1.1672	1.3603	0.4527
3000	1.408	1.2166	1.4585	0.4562

* $(M_0)_{T \leqslant 1600} \approx 0.0007T - 0.20.$

** $M_1 = \dfrac{(T - 298.2)^2}{2T}.$

*** $M_2 = \dfrac{T^2}{6} + \dfrac{298.2^3}{3T} - \dfrac{298.2^2}{2} = \dfrac{T^2}{6} + \dfrac{8\,835\,400}{T} - 44\,450.$

**** $M_{-2} = \dfrac{(T - 298.2)^2}{2 \times 298.2^2 T^2} = \dfrac{(T - 298.2)^2}{177\,800 T^2}.$

of the values computed according to a_3 and a_4, a_4 and a_5, respectively, as the values of ΔG°_{1100} and ΔG°_{1500}.

Equation (13.87) for the process being considered acquires the form

$$\Delta G^\circ_T = 49\,260 - 51.16T - T(16.249M_0 - 17.930 \times 10^{-3}M_1 + 4.276 \times 10^{-6}M_2)$$

We take the values of M_0, M_1 and M_2 from Table 23. The results of the calculations are given below:

T	700	1 100	1 500
ΔG°, cal/mol:			
First approximation	13 448	−7 016	−27 480
Second approximation	11 253	−14 134	−41 187
Third approximation	11 683	−12 396	−36 226
Temkin-Shwartsman method	11 575	−12 333	−36 531
Accurate calculations	11 437	−12 563	−36 869

Certain Laws. Gaseous substances have the greatest entropy; therefore ΔS for a chemical reaction (especially ΔS°_{298} and ΔS°_T) is determined first of all by the change in the volume ΔV in the process. It will be the greater, the more considerable is the jump of the change Δn^g in the number of moles of the gaseous reagents. We shall choose the heat effect — the most available parameter — as the quantity characterizing the feature of a process. We shall assume in a first approximation that the relationship $\Delta S = \varphi(\Delta n^g, \Delta H)$ has the form

$$\Delta S \approx a\Delta n^g + b\Delta H + c \qquad (13.89)$$

where a, b and c are constants.

In this expression, $c \neq 0$, because when $\Delta n^g = 0$ and $\Delta H = 0$ in the general case $\Delta S \neq 0$.

Introducing expression (13.89) into Eq. (5.22), we get the following approximate relationship after transformations:

$$\Delta G \approx A\Delta H + B \qquad (13.90)$$

where ΔG and ΔH are related to one g-equiv ($\Delta n^g = \text{const}$). This expression, which is an example of the second method of comparative calculations, is used in the form of the approximate relationship [B45]

$$\Delta G^\circ_{298} \approx A\Delta H^\circ_{298} + B \qquad (13.91)$$

to calculate chemical affinity in the absence of the values of the reagent entropies. The application of expression (13.91) is illustrated by Fig. 179 for the example of nitrates. The coefficients A and B in expressions (13.90) and (13.91) characterize a given group of

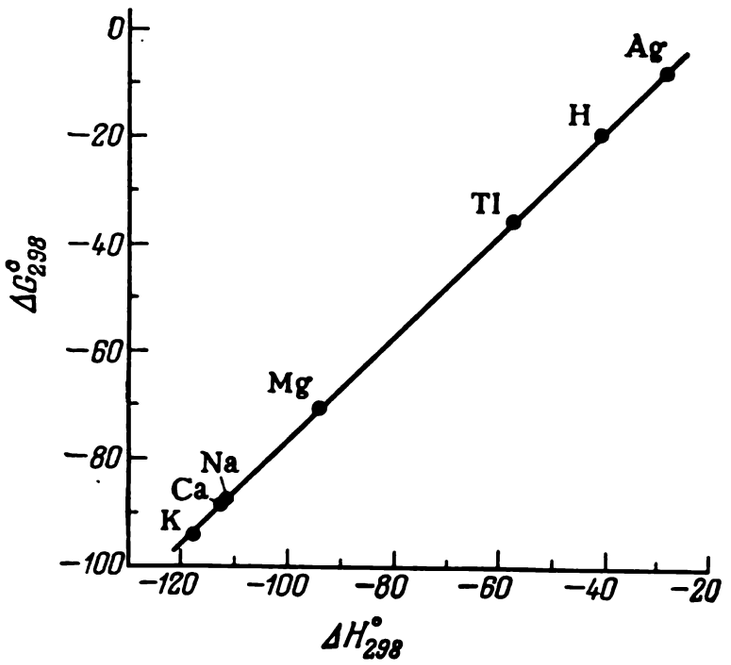


Fig. 179. Relationship between ΔH°_{298} and ΔG°_{298} (in kcal/g-equiv) for the formation of nitrates

substances. Thus, for the process

$$\frac{1}{m}\,\mathrm{El(c)} + \frac{1}{2}\,\mathrm{N_2(g)} + \frac{3}{2}\,\mathrm{O_2(g)} = \frac{1}{m}\,\mathrm{El(NO_3)_n(c)}$$

corresponding to Fig. 179, we have $A = 0.981$ and $B = 21.42$. With a certain loss of accuracy, the approximate equation

$$\Delta G^\circ_{298} \approx 0.986\,\Delta H^\circ_{298} - 9.4\,\Delta n^g$$

which compares the gramme-equivalent characteristics of substances, can be applied for any objects.

Returning to expression (13.89) and ignoring the second and third terms of its right-hand side, we get

$$\Delta S \approx a\Delta n^g \qquad (13.92)$$

If we assume that $a = 23$ in expression (13.92), we get N. Kobozev's rule (1948), which can be stated as follows: entropy changes by about the same value whether one mole of a substance is formed by vaporization of a liquid, i.e. as a result of a phase transformation, or by a reaction, i.e. as a result of a chemical transformation. Considering this rule approximate, we must also bear in mind that a depends on the nature of the reagents (for example for gaseous nitrogen oxides $a = 32.5 + 3.5$ e.u.), and that the approximate constancy of the molar entropy of vaporization relates only to the quantity $(\Delta S_{vap})_{n.b.p.}$, but neither to $(\Delta S^\circ_{vap})_{298}$, nor moreover to $(\Delta S_{vap})_{298}$ in equilibrium conditions (see Fig. 68, p. 242).

Naturally, everything said in this section does not relate to processes in which $\Delta S \neq 0$, although $\Delta V \approx 0$, for instance to reactions of isomerization (see p. 488).

Expressions of the following form can also be used in addition to expression (13.90):

$$\Delta Y_{II} \approx A\Delta Y_I + B \tag{13.93}$$

$$\Delta Y'' \approx A\Delta Y' + B \tag{13.94}$$

and

$$\Delta Y_N \approx A\Delta Y_M + B \tag{13.95}$$

in which $Y = S$ or G and which can be considered as the extension of expressions such as (13.69), (13.70) and (13.71) from a substance to a process.

Figure 180 gives an example of expression (13.93), and Fig. 181 (line *I*), of expression (13.95). The separate plotting of data for similar substances increases the accuracy of the results. For expression

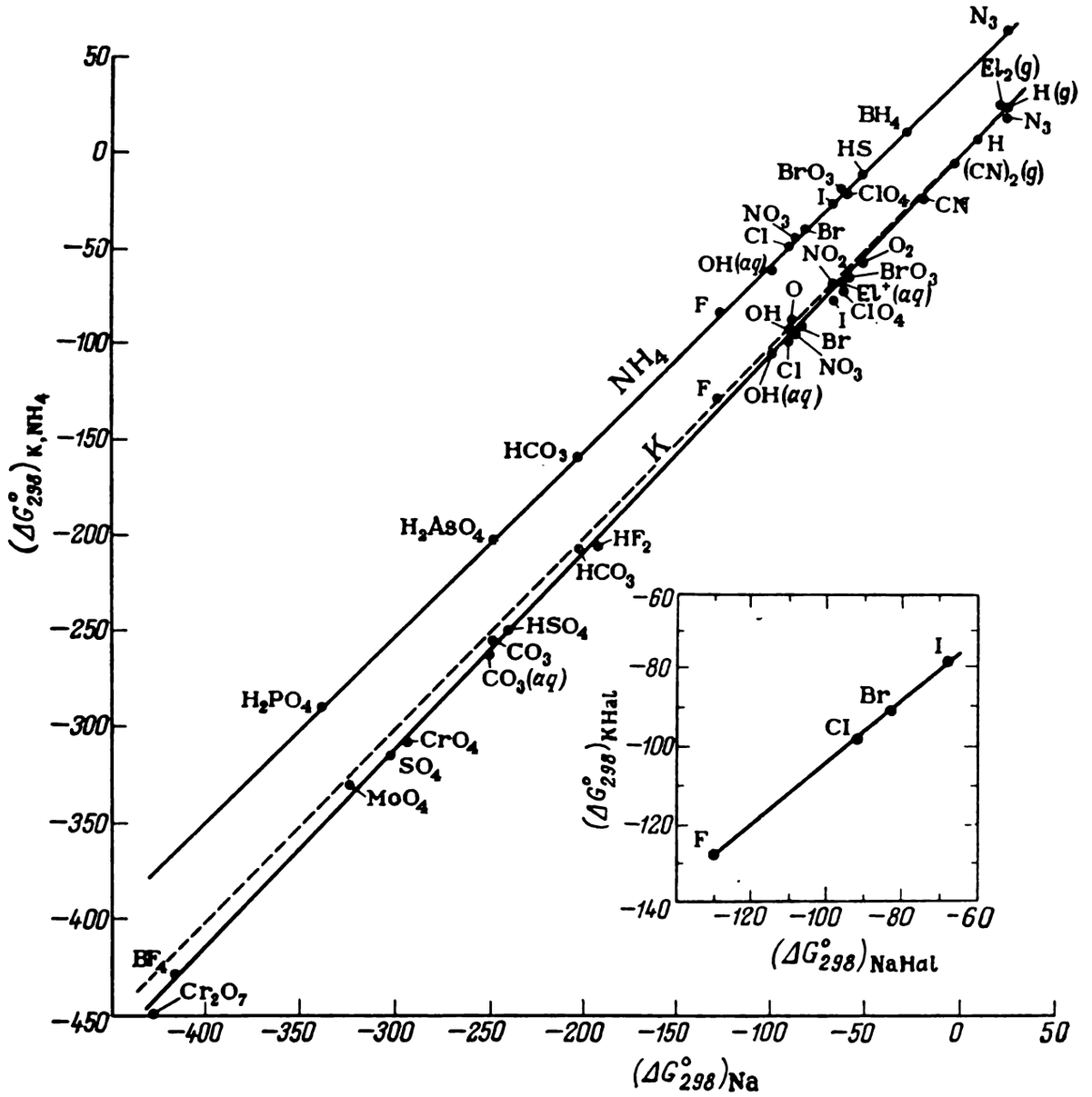


Fig. 180. Relationship between ΔG°_{298} of formation of selected compounds of sodium (*I*), potassium and ammonium (*II*). The relevant radicals are indicated opposite the respective points

(13.93), this is illustrated by the graph in the bottom right-hand corner of Fig. 180.

The correctness of expressions (13.93) and (13.95) for additive properties (for example for higher homologues) is obvious — the points for a consecutive series of substances (or reactions) on the relevant straight lines will be equally spaced.

Figure 182 indicates directly the diagonal similarity of lithium and magnesium: all the points obtained for different lithium-

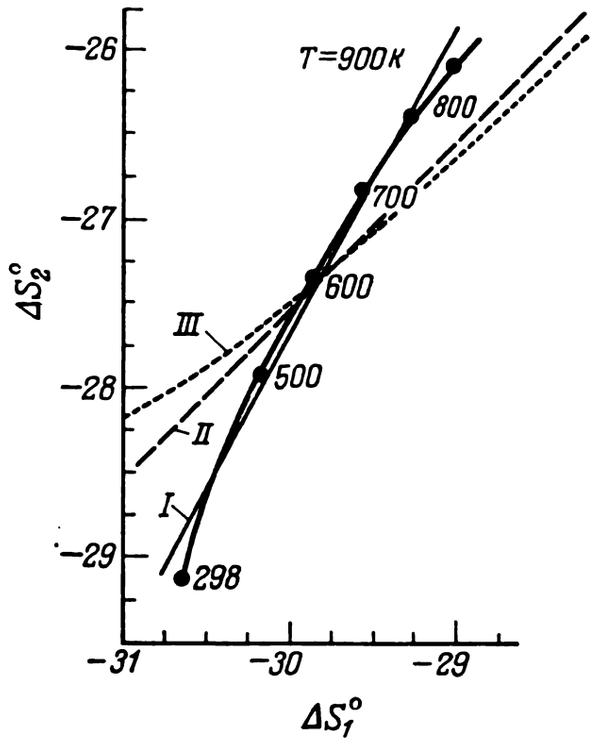


Fig. 181. Relationship between ΔS° in the reactions $MgO + 2HF = MgF_2 + H_2O(g)$ (*1*) and $MgO + 2HCl = MgCl_2 + H_2O(g)$ (*2*):

I — by expression (13.95); *II* — by expression (13.95) with $A = 1$ ($B = 2.5$); *III* — by expression (13.95) with $B = 0$ ($A = 0.917$)

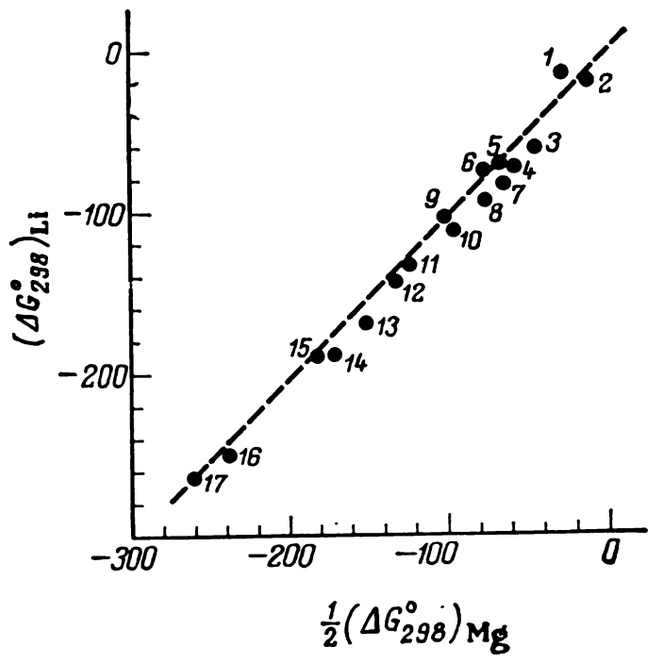


Fig. 182. Relationship between ΔG°_{298} (in kcal/g-equiv) of formation of magnesium and lithium compounds:

1 — $Mg_3N_2(c)$ and $Li_3N(c)$; *2* — $MgH_2(c)$ and $LiH(c)$; *3* — $MgI_2(c)$ and $LiI(c)$; *4* — $Mg^{2+}(aq)$ and $Li^+(aq)$; *5* — $MgO_2(c)$ and $Li_2O_2(c)$; *6* — $MgO(c)$ and $Li_2O(c)$; *7* — $MgBr_2(c)$ and $LiBr(c)$; *8* — $MgCl_2(c)$ and $LiCl(c)$; *9* — $Mg(OH)_2(c)$ and $LiOH(c)$; *10* — $Mg(NO_3)_2(c)$ and $LiNO_3(c)$; *11* — $MgCO_3(c)$ and $Li_2CO_3(c)$; *12* — $MgF_2(c)$ and $LiF(c)$; *13* — $MgSO_4(c)$ and $Li_2SO_4(c)$; *14* — $MgSiO_3(c)$ and $Li_2SiO_3(c)$; *15* — $MgTiO_3(c)$ and $Li_2TiO_3(c)$; *16* — $Mg_2SiO_4(c)$ and $Li_4SiO_4(c)$; *17* — $MgAl_2O_4(c)$ and $LiAlO_2(c)$

and magnesium-containing substances are close to the bisector of the quadrant angle which the expression

$$(\Delta G^\circ_{298})_{Li} \approx 0.5\ (\Delta G^\circ_{298})_{Mg}$$

corresponds to, i.e. indicate practically the same chemical affinity (in kcal/g-equiv). The insignificant displacement of most of the points to the right and downward corresponds to the more clearly expressed basic properties of magnesium compounds in comparison with those of lithium.

For very close processes (for example similar reactions of higher isostructural analogues), the coefficients in expression (13.93) are $A \approx 1$ and $B \approx 0$, i.e. $\Delta Y_{II} \approx \Delta Y_I$. [The same relates to expression (13.95).] In particular, the constancy of ΔS° in reactions of the same type can be illustrated by the reactions

$$MeSO_4 = MeO + SO_2 + \frac{1}{2}O_2 \quad \text{and} \quad MeCO_3 = MeO + CO_2$$

Assuming that $\Delta S^\circ_{298} = 68.5$ for the first of them, we shall find that this value fluctuates within the limits of ± 3 e.u. for nine sulphides. For the second reaction, we shall get a deviation (for 12 studied reactions) less than ± 1 e.u. with the mean value of ΔS°_{298} equalling 12.3.

We can also use the quantities ΔS°_a for a given group of compounds without introducing corrections for the different subgroups in the group. This permits us to considerably expand the reactions which can be calculated. For instance, instead of using the mean values of ΔS°_a separately for MeF, MeCl, MeBr and MeI, we can adopt one mean value of ΔS°_a for all the halides MeHal. Indeed, assuming that $\Delta S^\circ_a = -58.37$ e.u. for 38 compounds of the type MeHal and computing the values of ΔS° by Eq. (13.66), we shall find that for 17 substances for which the values of ΔH°_{298} and ΔG°_{298} are known, the discrepancy between the calculated and experimentally found changes in the Gibbs energy is less than 0.6 kcal.

With such a coincidence, we can predict the missing values of ΔG°_{298} and correct the inaccurate values of ΔH°_{298}, because for any reaction of a given type we have $298.2\Delta S^\circ_{298} = \Delta H^\circ_{298} - \Delta G^\circ_{298} \approx$ $\approx$ const. (The constancy of ΔS°_{298} for a given group of compounds corresponds to Kapustinsky's and Yatsimirsky's entropy additivity rule.)

Everything said above holds not only for the standard, but also for any temperature. From the constancy of ΔS° for all reactions of the same type, it follows that $\partial \Delta G^\circ / \partial T$ is also equal for them. This, in turn, denotes the equality of the coefficients of equal powers of the temperature for reactions of the same type, i.e. Δa, Δb, etc. Therefore, the values of ΔC_p should also be equal at the same temperature and vary identically with a change in temperature. Consequently, for any temperature

$$(\Delta G^\circ_{II} - \Delta G^\circ_I)_{T_1} = (\Delta H^\circ_{II} - \Delta H^\circ_I)_{T_1} =$$

$$= (\Delta G^\circ_{II} - \Delta G^\circ_I)_{T_2} = (\Delta H^\circ_{II} - \Delta H^\circ_I)_{T_2} = \ldots$$

where the subscripts I and II correspond to two reactions of the same type, and T_1 and T_2 to any two temperatures.

Knowing the relationship $\Delta H^\circ = \varphi(T)$ or $\Delta G^\circ = \varphi(T)$ for one reaction, we can use the value of ΔH° or ΔG° for one temperature to find these relationships for other reactions of the same type.

If we assume in the linear expressions (13.90), (13.91), (13.93)-(13.95) that $A \approx 1$ and $B \approx 0$ even for very similar reactions, however, this nevertheless leads to a certain loss of accuracy. This can be seen from Fig. 181 : line *II* corresponds to the condition $A \approx 1$, i.e. to constancy of the difference $\Delta Y_N - \Delta Y_M$ (in the given case to its independence of temperature); line *III* corresponds to the condition $B \approx 0$, i.e. to constancy of the ratio $\Delta Y_N : \Delta Y_M$ (in the given case to its independence of temperature).

Chapter 14

EQUILIBRIUM TRANSFORMATION

14.1. DIRECTION OF A PROCESS

The possibility of conducting a process *in principle* is determined by the sign of ΔG: if in given conditions $\Delta G < 0$, a reaction is possible; if $\Delta G > 0$, a reaction is impossible; if $\Delta G = 0$, the system is in equilibrium (see Sec. 5.1). The value of ΔG (when $\Delta G < 0$) permits us to establish how far the system being studied is from the state of equilibrium.

If a reaction does not proceed at $\Delta G \ll 0$, this only indicates the need to overcome the obstacles inhibiting the reaction (low temperatures as a rule) and bring the system out of the state of false equilibrium. The presence of an energy barrier hindering a process is the cause of the chemical inertness of substances in definite conditions; this inertness often ensures the existence of substances.

Therefore, a reaction may not proceed either as a result of closeness to the state of equilibrium or as a result of inhibition. To cause a reaction, in the first case we must change the conditions in which it proceeds, and in the second its rate. For example, although for the reaction

$$H_2 + \frac{1}{2} O_2 = H_2O(lq)$$

the value of ΔG_{298} is less than zero at $t = 25\,°C$, no water forms. But it is sufficient to introduce an appropriate catalyst, and the reaction will proceed at a high rate and practically to the end. The action of a catalyst, however, cannot change the values of ΔG, $\Delta G°$ and K_a; these quantities depend only on the initial and final states of the relevant system.* This is why the theory which adopted the rate of a reaction as the measure of affinity was erroneous.

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* Strictly speaking, the postulate on the constancy of equilibrium in the presence of a catalyst relates to heterogeneous catalysis, because in a homogeneous system the activity of the reagents may change in the presence of other substances, particularly a catalyst if its concentration is sufficiently high.

In an inhibited system, a reaction may also be initiated by heating, which functions like a lubricant helping to overcome friction. For instance, a thermite mixture may exist for an infinitely long time as long as the aluminium is protected against oxidation, but insignificant local heating results in an energetic ($\Delta G^\circ_{298} = -204\,000$ cal/mol) exothermic reaction .*

Without a knowledge of thermodynamics, we cannot say what part of an effect observed in each separate case is due to a change in the rate and what part to a displacement of equilibrium.

If in true equilibrium there is a relationship between a force and its action, in false equilibrium there is no such relationship. Therefore, the displacement of false equilibrium is attended by an irreversible process (for example an explosion), whereas a change in true equilibrium must always be a reversible process. (It should be remembered that the Le Chatelier principle can be applied only to systems in true equilibrium.)

Therefore, the constancy of a system over time is not sufficient to tell whether or not true equilibrium takes place in a system.

True equilibrium is achieved at any activities (concentrations) in both the forward and reverse course of a reaction. Hence, if a given state is reached by either way of conducting a reaction, the system is in true thermodynamic equilibrium ** (Fig. 183*a*).

Inspection of Fig. 183 also shows that formal interpretation of the conditions of the possibility of a process may lead to erroneous conclusions. Indeed, although $G_a < G_c$, the transition from state *c* to state *a* is impossible. The same can be said about the condition of equilibrium : any two states of the system corresponding to a horizontal line in Fig. 183 (for instance points *a* and *b*) characterize non-equilibrium states of the system, although their Gibbs energies are identical. Such misunderstandings are prevented if we proceed from the conditions $dG_{p,T} < 0$ and $dG_{p,T} = 0$, because when we go over to infinitely small displacements, we cannot avoid point *O*.

When ΔH and ΔS have different signs in a given process, it is irreversible : at $\Delta H < 0$ and $\Delta S > 0$ it must proceed in the direction of the products, and at $\Delta H > 0$ and $\Delta S < 0$ in the direction of the reactants.

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* A substance whose decomposition is connected with diminishing of the Gibbs energy may be unstable, or even explosive, if together with $\Delta G \ll 0$, we also have $\Delta H \ll 0$. Here decomposition proceeds instantaneously (practically adiabatically), which leads to intensive heating and to a tremendous increase in the volume of the liberated gases. Such substances include pyroxyline, nitroglycerin, and tetranitropentaerythritol. The condition that $\Delta G \ll 0$ cannot be sufficient for a conclusion on the explosiveness of a given substance, because the values of ΔH are usually so small that the heat liberated in decomposition is not sufficient for an explosion.

** We must remember the difference between chemical and thermodynamic reversibility. The former only means that a reaction simultaneously proceeds in opposite directions.

If the substances being studied can react in several directions, for example in two, which the values of ΔG_1 and ΔG_2 correspond to (and $\Delta G_1 < \Delta G_2$), this does not yet mean that the first reaction is easier to accomplish in any conditions than the second, because ΔG_1

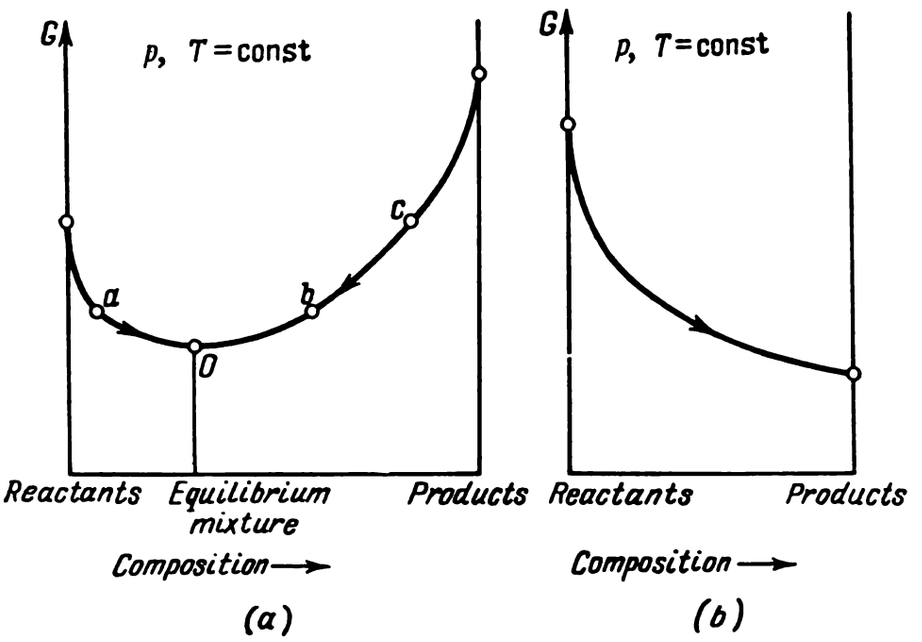

Fig. 183. Diagram showing change in Gibbs energy in a process: *a*—reversible; *b*—irreversible

and ΔG_2 are *different* functions of p and T. With a growth in the difference between the values of ΔG for the possible reactions, this conclusion will lose its force. In addition, at $\Delta G < 0$ a reaction does not always proceed in a given direction. The transformation of the reactants into other products may be connected with a still greater lowering of the Gibbs energy; in other words, the transformation of the products of the first reaction into those of the second will be spontaneous. Therefore, when $\Delta G < 0$, a system is "protected" only from a transition to the initial state. If, despite the growth in the Gibbs energy, a reaction nevertheless proceeds, this means that one or more other reactions are proceeding together with it; the lowering of the Gibbs energy in it (them) is greater than its growth for the given reaction, and as a result the total process is connected with a decrease in the Gibbs energy.*

When a reaction is thermodynamically impossible ($\Delta G > 0$) in given conditions, we can create other conditions in which the reaction will proceed in the required direction by correspondingly choosing the concentrations of the reagents without changing p and T.

* For the calculation of complex equilibria see Sec. 14.4.

Can we assess the possibility of a given reaction according to the value of ΔG°? This is an important question, because it is much easier to calculate ΔG° than ΔG. Regardless of how close the conditions of a reaction are to standard ones, we can make the following remarks.

1. When at a given temperature $\Delta G^\circ \ll 0$ and in accordance with Eq. (13.8) the equilibrium constant is very great, the reaction is possible in principle not only in standard, but also in any conditions: to change the sign of ΔG, we should increase the absolute value of the first term of the right-hand side of Eq. (13.5) by an amount that is unattainable in practice.

This conclusion holds particularly for a reaction of formation of compounds from simple substances. We can therefore speak of the thermodynamic stability of a compound ($\Delta G^\circ \ll 0$), i.e. of the possibility of its formation from simple substances. For example, we can consider that the synthesis of saccharose from carbon, oxygen and hydrogen, for which $\Delta G^\circ_{298} = -369\,180$ cal/mol, is possible in principle.

Another example is the reaction

$$Zn + \frac{1}{2} O_2 = ZnO$$

For this reaction, $\Delta G^\circ_{298} = -76\,640$ cal/mol; therefore zinc is easily oxidized even at $p_{O_2} = 0.000\,01$ atm. Gold, for example, is more stable, while magnesium is less stable than zinc, therefore the latter is displaced by magnesium from solutions of its salts. Indeed, for Au_2O_3 we have $\Delta G^\circ_{298} = 18\,800$, and for MgO we have $\Delta G^\circ_{298} = -136\,980$ cal/mol.

2. When $\Delta G^\circ \gg 0$, a reaction will not proceed to an appreciable extent. Moreover, when the value of ΔG° is very great, we can say with certainty that conditions cannot be created which will favour the proceeding of a reaction. Thus, for the process

$$N_2(g) + 2H_2O(lq) = NH_4^+(aq) + NO_2^-(aq)$$

We have $\Delta G^\circ_{298} = 85\,546$ cal/mol. Such a great fugacity f_{N_2} corresponds to this value that the above process is practically impossible.

If notwithstanding the fact that for a given substance $\Delta G^\circ_{298} \gg 0$ it does not decompose, its decomposition into simple substances is kinetically retarded. This case is of special interest for chemists. It means that a given substance cannot be prepared by *direct synthesis*. Indeed, C_2H_2, N_2O_3, Cl_2O_7, and many other compounds (particularly boranes and silanes) can be obtained only indirectly.

3. If the numerical value of ΔG° is not great, then regardless of its sign, no conclusions can be made on the direction of a process. It is only clear that a reaction can be conducted in the desired

direction under the corresponding conditions; in other words, there is a possibility of changes in either direction in the system. Thus, if for the synthesis of ammonia $\Delta G^\circ_{673} = 5780$ cal/mol (the process can be conducted at 400 °C with the aid of a catalyst), we can speak of the thermodynamic instability of ammonia at atmospheric pressure and the indicated temperature. But for the reaction of synthesis of ammonia $\Delta V < 0$, and by the equation $(\partial \Delta G/\partial p)_T = \Delta V$ following from Eq. (5.25) we should expect a decrease in ΔG (and not in ΔG°!) at high pressures. Indeed, the synthesis of ammonia in practice is connected with the use of high pressures.

Here is another example: zinc and some other metals displace hydrogen from acids at $p = 1$ atm, whereas at higher pressures the reaction proceeds in the reverse direction.

4. When $\Delta G^\circ = 0$ ($K_a = 1$), the reactants must undergo a considerable transformation for an equilibrium state to set in in a system.

When $K_a = 1$, the equilibrium of reactions is displaced toward their products.

The conclusions that can be made by analysing the values of ΔG°_{298} coincide with the majority of the above considerations for ΔG°. It should only be remembered that the temperature at which the vast majority of chemical processes occur is considerably higher than 25 °C. The values of ΔG°_{298} given in the relevant tables show the instability of organic compounds, especially of hydrocarbons. Organic substances are thermodynamically unstable not only relative to simple substances, i.e. carbon, hydrogen, oxygen, etc., but also relative to the products of oxidation — CO_2, H_2O, etc.

Systematization of the values of ΔG°_{298} for hydrocarbons resulted in a number of important conclusions. Thus, it was established that the instability of isomers in comparison with normal hydrocarbons becomes more sharply expressed with an elevation of temperature. This is explained by diminishing of the entropy in isomerization processes. For instance, an equilibrium mixture of the five hexanes should contain about 1.5% of normal hexane at 298 K, and over 30% at 1000 K. To a certain extent, this is explained by the predomination of normal hydrocarbons over their isomers in natural petrol and other petroleum products (see p. 596f). The relative stability of a number of gaseous hydrocarbons can be judged according to the approximate data given in Fig. 184.

The values contained in tables of standard changes in Gibbs energies can thus serve as the starting point for solving many problems involving the chemical equilibria of reactions in *actual* conditions.

When the absolute value of ΔG° is very great, even a big error cannot affect the correctness of our assessment of the possibility or impossibility of a process. At low values of ΔG°, however, the

authenticity of $\Delta G°$ becomes very important for a proper appraisal of whether or not a process is possible. Even if we assume that all the values of $\Delta G°$ are known with the same accuracy, we cannot draw definite boundaries for the values of $\Delta G°$ outside of which we could establish the possibility or impossibility of a process in preset conditions .*

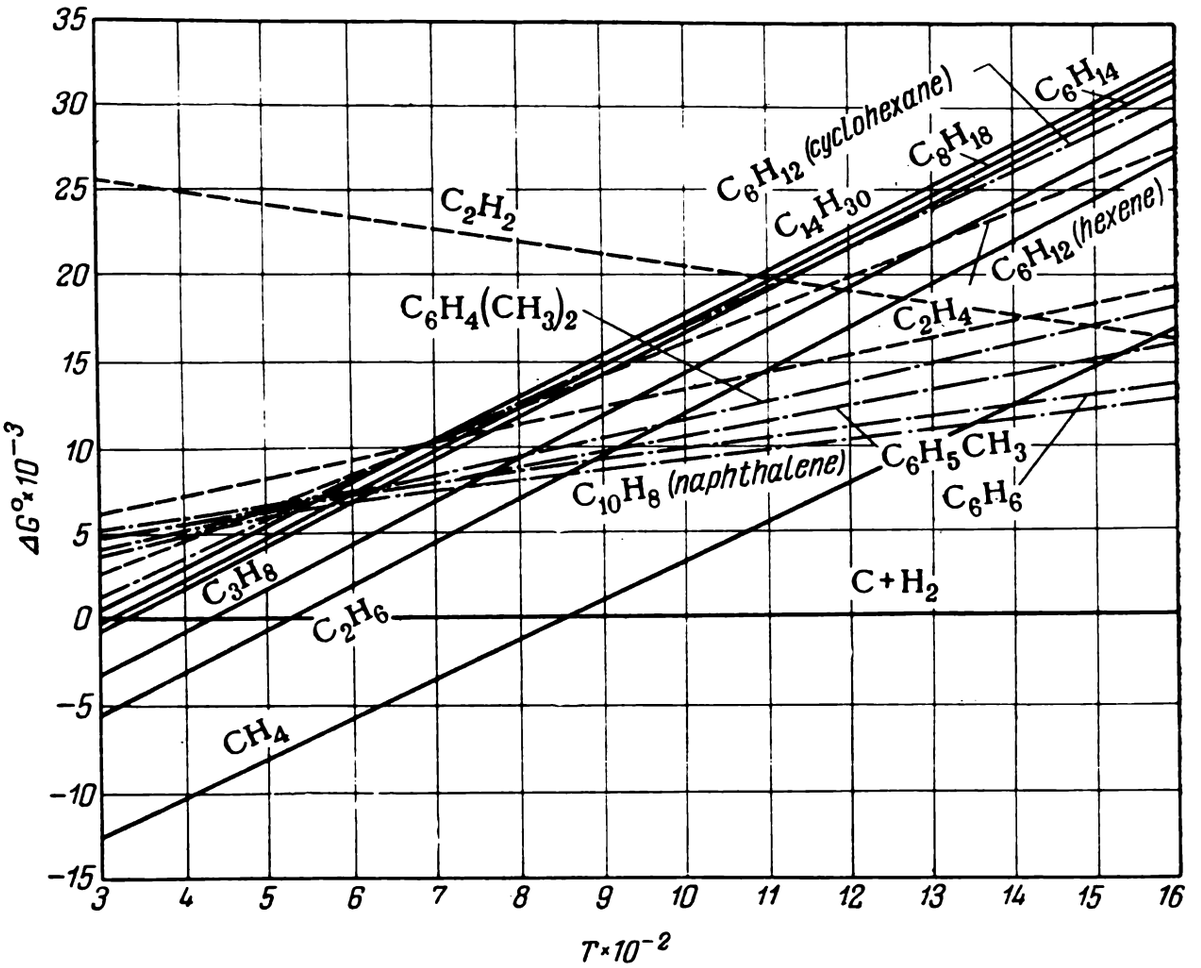

Fig. 184. Approximate values of $\Delta G°$ (in cal/g-atom) for the formation of selected hydrocarbons from simple substances [B79].

(See Example 3)

Example 1. Use the values of $\Delta G°_{298}$ (see Table 14) to assess the possibility of preparing aniline from benzene by (1) nitration with the following reduction of the nitrobenzene (disregard the values of $\Delta G°_{298}$ for condensation of the benzene and the transition from the dilute to the concentrated acid); (2) chlorination with the following action of ammonia on the chlorobenzene; and (3) the direct action of ammonia.

Solution. 1. The process involves the consecutive proceeding of the reactions

$$C_6H_6(lq) + HNO_3(aq) = H_2O(lq) + C_6H_5NO_2(lq)$$

* Sometimes the very *rough* value of $\Delta G° \leqslant 10\,000$ cal/mol is indicated (see, for example, [A10, B98]).

and

$$C_6H_5NO_2(lq) + 3H_2 = 2H_2O(lq) + C_6H_5NH_2(lq)$$

According to the data of Table 14 we have $\Delta G^\circ_{298} = -24\,803$ cal/mol for the first and $\Delta G^\circ_{298} = -112\,726$ cal/mol for the second.

2. The process involves the consecutive proceeding of the reactions

$$C_6H_6(lq) + Cl_2(g) = HCl(g) + C_6H_5Cl(lq)$$

and

$$C_6H_5Cl(lq) + NH_3(g) = HCl(g) + C_6H_5NH_2(lq)$$

for which we find $\Delta G^\circ_{298} = -31\,180$ and $\Delta G^\circ_{298} = -4480$ cal/mol, respectively.

3. The process consists in the reaction

$$C_6H_6(lq) + NH_3(g) = C_6H_5NH_2(lq) + H_2(g)$$

for which $\Delta G^\circ_{298} = 9900$ cal/mol.

An analysis of the results of the calculations shows that the first two methods are connected with a decrease in the Gibbs energy, even if we take into account the error of the calculations due to the above assumptions and the possible inaccuracy of the values of ΔG°_{298} for aniline, chlorobenzene and nitrobenzene. The fact that in practice metallic iron and dilute hydrochloric acid are most frequently used as the reducing agent (the first process) can also hardly have an appreciable effect.

For the third process, $\Delta G^\circ_{298} > 0$, and therefore equilibrium should be shifted in the direction of benzene and ammonia.

The first and second processes are widely used in the chemical industry, while attempts to carry out the third have not been successful.

Example 2. In the cracking of hydrocarbons of the methane series, the following reactions are of the greatest significance:

$$C_nH_{2n+2} = C_nH_{2n} + H_2 \qquad (1)$$

and

$$C_{m+n}H_{2(m+n)+2} = C_mH_{2m+2} + C_nH_{2n} \qquad (2)$$

and the following approximate equations were proposed to calculate ΔG° for them:

$$\Delta G^\circ = 33\,400 - 500n - 27.9T - 1.0nT \qquad (a)$$

and

$$\Delta G^\circ = 18\,700 - 500n - 26.9T - 1.0nT \qquad (b)$$

By analysing these equations, show:

(1) what kind of cracking is most probable;

(2) whether the cracking of hexane is possible by Eq. (1) at 600 °C;

(3) what the size of a molecule should be for decomposition according to Eq. (1) to be sufficiently considerable at 400 °C;

(4) for which of these reactions the size of a molecule is of the greatest significance;

(5) whether the probability of decomposition of a hydrocarbon into two equal parts changes with a growth in the size of a molecule;

(6) what mechanism of decomposition according to Eq. (2) is the most probable;

(7) the validity of the following rule: in the cracking of alkanes two unequal molecules are formed, the larger one being an unsaturated, and the smaller one a saturated compound.

Solution. 1. The thermodynamically most probable reaction is not dehydrogenation, but cracking according to Eq. (2), because at the same temperature $\Delta G_2^\circ < \Delta G_1^\circ$.

2. Inserting into Eq. (a) the values of $n = 6$ and $T = 873.2$, we get $\Delta G^\circ = 800$ cal/mol; therefore at 600 °C the cracking of hexane into hexene and hydrogen becomes possible.

3. Inserting into Eq. (a) the value of $T = 673.2$, we get the equation

$$\Delta G^\circ = 14\,620 - 1173n$$

from which it follows that at the indicated temperature cracking becomes possible only for hydrocarbons with a molecular weight greater than that of $C_{13}H_{28}$.

4. The size of a molecule of the hydrocarbon subjected to cracking is of great importance with the second mechanism of the process, because the terms containing n in Eq. (b) form a greater part of ΔG° for any temperature than those in Eq. (a).

5. With an increase in the chain length, the probability of central breakage of a molecule grows, because a growth of n is attended by a diminishing of ΔG°, and therefore the constant of the corresponding equilibrium increases.

6. The total number of variants of decomposition according to Eq. (2) equals $(m + n - 2)$. The value $m + n - 1$, which is the maximum possible (because it corresponds to the greatest molecular weight of an alkene) at the same time, as can be seen from the equation $\Delta G^\circ = \varphi(T)$, corresponds to the minimum of all the possible values of ΔG°. Therefore, cracking of alkanes according to the reaction

$$C_{m+n}H_{2(m+n)} = C_{m+n}H_{2(m+n-1)} + H_2$$

is the most probable (the main product of decomposition of the higher alkanes is obviously methane). The data given below confirm these conclusions for hexane:

$$C_6H_{14} = CH_4 + C_5H_{10} \qquad \Delta G^\circ = 16\,200 - 31.9T$$
$$C_6H_{14} = C_2H_6 + C_4H_8 \qquad \Delta G^\circ = 16\,700 - 30.9T$$
$$C_6H_{14} = C_3H_8 + C_3H_6 \qquad \Delta G^\circ = 17\,200 - 29.9T$$
$$C_6H_{14} = C_4H_{10} + C_2H_4 \qquad \Delta G^\circ = 17\,700 - 28.9T$$

7. The validity of the indicated rule follows from a consideration of the solution of the preceding problems.

Example 3. Answer the following questions by analysing the data of Fig. 184.

1. Which hydrocarbon is the most stable?

2. How does the stability of hydrocarbons change with temperature?

3. How can the fact that considerable decomposition of $C_{14}H_{30}$ can be detected in distillation at $p = 1$ atm and $t < 490\,^\circ C$ be explained?

4. Can benzene be transformed into acetylene at $T = 1000$ K?

5. In which direction should the reaction $3C_2H_4 = C_6H_{12}$ (hexene) proceed at $T = 1000$ K? Find the equation $\Delta G^\circ = \varphi(T)$ and indicate the temperature for which it is expedient to find a catalyst for this process.

6. Which hydrocarbons are relatively more stable at elevated temperatures: alkanes, alkenes, cyclanes or aromatic hydrocarbons? Also consider the influence of unsaturation on the thermodynamic stability of aliphatic compounds.

Solution. 1. Methane is the most stable, because the line $\Delta G^\circ = \varphi(T)$ for it is below the straight lines of the other hydrocarbons for all temperatures (except very high ones).

2. The stability of all the hydrocarbons drops with elevation of the temperature; moreover, no hydrocarbon at $T > 850$ K is thermodynamically stable relative to its simple substances. An exception is acetylene: although it is unstable relative to its simple substances (and at low temperatures also relative to hydrocarbons), its instability diminishes somewhat with elevation of the temperature.

3. Since the values of ΔG° for $C_{14}H_{30}$ are not only greater than the Gibbs energy of the simple substances, but also exceed ΔG° for the very simple alkanes for any temperatures, these hydrocarbons are not stable even at ordinary temperatures.

4. Transformation is impossible, because

$$\Delta G^\circ_{1000} = (3 \times 2 \times 20\,500 - 6 \times 10\,000) \gg 0$$

5. Seeing that $\Delta G^\circ_{1000} = 6 \times 16\,200 - 3 \times 2 \times 13\,600 = 15\,600$ cal/mol, at the indicated temperature the reaction tends to proceed toward the decomposition of hexene, and not the polymerization of ethene.

We compile a system of equations $\Delta G^\circ = a + bT$ [Eq. (13.15)]:

$$\Delta G^\circ_{1000} = 15\,600 = A + 1000B \text{ and } \Delta G^\circ_{500} = -9000 = A + 500B$$

whence $A = -33\,600$ and $B = 49.2$. Therefore, the required equation has the form $\Delta G^\circ = -33\,600 + 49.2T$, and ΔG° becomes negative at $T \leqslant 680$ K, i.e. a catalyst should be selected for $T < 680$ K.

6. Alkanes and cyclanes are more stable at low temperatures, and aromatic compounds and alkenes (with respect to the former) at high temperatures. This relationship determines the mutual transformation of the indicated compounds at different temperatures.

To answer the second question, let us compare the straight lines (see Fig. 184) for C_2H_6, C_2H_4 and C_2H_2; although the influence of the double and triple bond for these substances is stronger, the same relationship should also exist qualitatively between the higher homologues. Ethane is the most stable at low temperatures, but at $T \geqslant 1090$ K it becomes less stable than ethene, and both of them are unstable with respect to their simple substances. Acetylene has the lowest stability up to 1420 K, and only above this temperature is it more stable. At the same time, acetylene never becomes really stable relative to its simple substances, because $\Delta G^\circ > 0$ for it within the range of temperatures covered by Fig. 184. For the temperature when ΔG° changes its sign, the value of ΔG° can be found by extrapolation. Before ΔG° becomes negative, however (which a temperature of about 4000 °C corresponds to), the hydrogen almost completely dissociates into atoms.

14.2. CALCULATION OF EQUILIBRIUM TRANSFORMATION

Assume that the following reaction proceeds:

$$b\mathrm{B(g)} + c\mathrm{C(g)} + d\mathrm{D(lq)} + \ldots = r\mathrm{R(g)} + s\mathrm{S(g)} + t\mathrm{T(c)} + \ldots$$

The equilibrium constant by Eq. (13.6) will therefore be

$$K_a = \frac{a_T^t f_R^r f_S^s \cdots}{a_D^d f_B^b f_C^c \cdots} \tag{14.1}$$

The fugacities of the gaseous components, strictly speaking, ought to be calculated by Eq. (8.9), but very scant data are available on the relationship $\bar{V}_i = \varphi(p, T, x)$. Without a great error, however,

we can use the fugacity rule expressed by Eq. (8.36) which in most cases holds up to comparatively high pressures. Let us agree to calculate f_i in the following by Eq. (8.36) or in accordance with Eq. (6.34) by the equation

$$f_i = p\gamma_i x_i \tag{14.2}$$

i.e. we shall consider that the gaseous phase is an ideal solution (see Sec. 8.4). In this connection, Eq. (14.1) can be given the following form :

$$K_a = \frac{a_T^t \cdots}{a_D^d \cdots} \frac{x_R^r x_S^s \cdots}{x_B^b x_C^c \cdots} \frac{\gamma_R^r \gamma_S^s \cdots}{\gamma_B^b \gamma_C^c \cdots} p^{(r+s+\cdots)-(b+c+\cdots)} = \frac{a_T^t \cdots}{a_D^d \cdots} K_x K_\gamma p^{\Delta n} =$$

$$= \frac{a_T^t \cdots}{a_D^d \cdots} K_n K_\gamma \left(\frac{p}{n_B + n_C + \ldots + n_R + n_S + \ldots + n_{in.g}} \right)^{\Delta n} \tag{14.3}$$

where

$$K_x = \frac{x_R^r x_S^s \cdots}{x_B^b x_C^c \cdots} \quad \text{and} \quad K_n = \frac{n_R^r n_S^s \cdots}{n_B^b n_C^c \cdots} = K_x (\Sigma n_i)^{\Delta n} \tag{14.4}$$

$$K_\gamma = \frac{\gamma_R^r \gamma_S^s \cdots}{\gamma_B^b \gamma_C^c \cdots} \tag{14.5}$$

$$\Delta n = (n_R + n_S + \ldots) - (n_B + n_C + \ldots)$$

$n_{in.g}$ = number of moles of the inert gas.

After finding the equilibrium constant by an appropriate method (see Chap. 13), we can use Eq. (14.3) to determine the equilibrium composition of the system. The content of each substance in equilibrium should be expressed by the initially taken number of moles of it and the number of moles of the substances that have reacted by the moment when equilibrium sets in. We find the equilibrium composition of the reaction mixture by introducing these quantities into Eq. (14.3) and solving it analytically or graphically.

14.2.1. Reactions in the Gaseous Phase

If all the reagents are gaseous, then Eq. (14.3) becomes

$$K_a = K_f = \frac{f_R^r f_S^s \cdots}{f_B^b f_C^c \cdots} = K_x K_\gamma p^{\Delta n} =$$

$$= K_n K_\gamma \left(\frac{p}{n_B + n_C + \ldots + n_R + n_S + \ldots + n_{in.g}} \right)^{\Delta n} \tag{14.6}$$

The quantity K_γ generally depends on temperature and pressure. This is explained by the different compressibility of gases at high pressures, i.e. by different numerical values of γ_i in Eq. (14.6). Since in calculating f_i by Eq. (14.2), it is assumed that the gas mixture is an ideal solution, K_γ does not depend on the composition. For very high pressures, this assumption may result in errors, especially for components whose concentration is not great; the errors may become appreciable when a mixture contains polar gases.

High Pressure. A graph of γ against π and τ (see Fig. 40, p. 192) is generally used to determine γ_i. The calculation of equilibrium with this graph is especially important in organic chemistry, where p-V-T-x-data are scant. Next K_γ is calculated by Eq. (14.5). If equilibrium is being calculated for a wide range of pressures and temperatures, it is expedient to construct a graph that would give the values of $K_\gamma = \varphi(p, t)$ for a given equilibrium. An example of such a graph is shown in Fig. 185, which also gives the fugacities of the mixture components (the nature of the change in f_i with pressure shows that in the given example K_γ diminishes with a growth in pressure).

Sometimes the value of K_γ may differ from unity even at a few atmospheres; and, conversely, at considerable pressures owing to the mutual compensation of the values of γ_i, the constant K_γ may approach unity. An example of the latter is the reaction

$$C_2H_4 + H_2O(g) = C_2H_5OH(g)$$

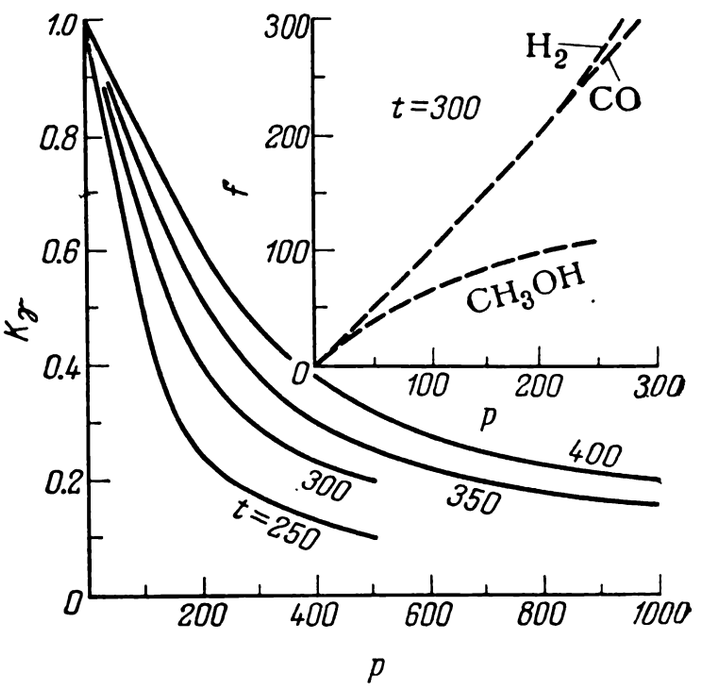

Fig. 185. Dependence of K_γ on pressure and temperature for the reaction $CO + 2H_2 = CH_3OH(g)$. (The pressure dependence of f for H_2, CO and CH_3OH is shown in the top right-hand corner)

Example 4. Find the yield of methanol at $t = 250\,°C$ and $p = 100$ atm for the reaction

$$CO + 2H_2 = CH_3OH(g)$$

if the initial mixture consists of one mole of CO and two moles of H_2. Assume that for this process

$$\Delta G^\circ = -17\,560 + 41.17T \log T - 13.4 \times 10^{-3}T^2 - 59.24T$$

Solution. From the equation $\Delta G^\circ = \varphi(T)$, we find $\Delta G^\circ_{523.2} = 6345$ cal/mol and from Eq. (13.8) we get $\log (K_a)_{523.2} = -2.6508$ and $(K_a)_{523.2} = 2.235 \times 10^{-3}$. [It was found from experiments conducted at low pressures that $(K_p)_{523.2} = 2.32 \times 10^{-3}$.]

We use the following scheme to calculate the yield:

Reaction	CO	$+ 2H_2$	$= CH_3OH$
Number of moles:			
in initial mixture	1	2	0
in equilibrium mixture	$1-y$	$2-2y$	y
total		$3-2y$	

By Eq. (14.6) we have

$$K_a = K_f = \frac{f_{CH_3OH}}{f_{CO} f_{H_2}^2} = \frac{n_{CH_3OH}}{n_{CO} n_{H_2}^2} K_\gamma \left(\frac{p}{n_{CO} + n_{H_2} + n_{CH_3OH}} \right)^{1-3}$$

where $K_\gamma = \gamma_{CH_3OH}/\gamma_{CO}\gamma_{H_2}^2$.

From Fig. 185 we find that $K_\gamma = 0.44$. Therefore

$$2.235 \times 10^{-3} = \frac{y}{(1-y)(2-2y)^2} \times 0.44 \left(\frac{100}{3-2y} \right)^{-2}$$

or

$$\frac{y(3-2y)^2}{4(1-y)^3} = 50.8$$

whence by trial and error we get $y \approx 0.8$, which corresponds to a methanol yield equal to $0.8 \times 100/(3 - 2 \times 0.8) = 57\%$.

The unreliability of the values of K_γ cannot be a source of considerable errors in the given case: even if we assume that $K_\gamma = 0.5$, this will change the result by about 1%.

Low Pressure. For low pressures and practically any temperatures, K_γ differs slightly from unity, because the activity coefficients can be assumed equal to unity. Consequently, Eq. (14.6) takes the form

$$K_a = K_f = K_p = \frac{p_R^r p_S^s \cdots}{p_B^b p_C^c \cdots} = K_x p^{\Delta n} =$$

$$= K_n \left(\frac{p}{n_B + n_C + \ldots + n_R + n_S + \ldots + n_{in.g}} \right)^{\Delta n} \qquad (14.7)$$

Example 5. The equilibrium constant of the reaction of oxidation of SO_2 to SO_3 at $T = 650$ K and $p = 1$ atm equals 629. Find the

composition of the equilibrium mixture if the mixture fed to the contact process consists of 7% of SO_2, 11% of O_2 and 82% of N_2.

Solution

Reaction	SO_2	$+ \frac{1}{2} O_2$	$= SO_3$
Number of moles:			
in initial mixture	0.07	0.11	$0(0.82N_2)$
in equilibrium mixture	$0.07 - y$	$0.11 - 0.5y$	$y(0.82N_2)$
total	$1 - 0.5y$		

By Eq. (14.7)

$$K_p = \frac{p_{SO_3}}{p_{SO_2}^{\frac{1}{2}} p_{O_2}} = \frac{n_{SO_3}}{n_{SO_2}^{\frac{1}{2}} n_{O_2}} \left(\frac{p}{n_{SO_2} + n_{O_2} + n_{SO_3} + n_{N_2}} \right)^{1-1.5}$$

or

$$629 = \frac{y}{(0.07 - y)(0.11 - 0.5y)^{\frac{1}{2}}} \left(\frac{1}{1 - 0.5y} \right)^{-0.5} = \frac{y\sqrt{1 - 0.5y}}{(0.07 - y)\sqrt{0.11 - 0.5}}$$

whence by trial and error we find $y = 0.0696$, i.e. the equilibrium mixture will contain $\frac{0.0696}{1 - 0.5 \times 0.0696} \times 100 = 7.13\%$ of SO_3, $\frac{0.07 - 0.0696}{1 - 0.5 \times 0.0696} \times 100 = 0.04\%$ of SO_2, $\frac{0.11 - 0.5 \times 0.0696}{1 - 0.5 \times 0.0696} \times 100 = 7.71\%$ of O_2 and 85.12% of N_2.

14.2.2. Reactions in Solutions

Since the activity of each of the reagents is a complicated function of the temperature and composition, and the relationship between it and the indicated parameters is simple only at the limit, the calculation of equilibrium in solutions is very complicated, and a number of simplifying assumptions are usually introduced.

If a solution can be considered ideal, the activities in accordance with the equation $a_i = x_i$ [Eq. (8.37)] are replaced with the mole fractions or, rather, with the ratio of the mole fractions in equilibrium, because the state of the pure liquid under a total pressure of 1 atm, and for solid reagents the state of the pure supercooled liquid in the same conditions are taken as the standard state at each temperature. This choice of the standard state for the solid components of a solution is due to the fact that the replacement of the activity of a component of a solution with a quantity proportional to the concentration holds, strictly speaking, only for

ideal solutions for which the additivity of the enthalpy is observed only at the same states of aggregation of the reagents.

Thus, for ideal solutions, Eq. (14.1) becomes

$$K_a = K_x = \frac{x_R^r x_S^s \cdots}{x_B^b x_C^c \cdots} = \frac{c_R^r c_S^s \cdots}{c_B^b c_C^c \cdots} \left(\frac{V}{n_B + n_C + \ldots + n_R + n_S + \ldots} \right)^{\Delta n} =$$

$$= K_c \left(\frac{V}{\Sigma n_i} \right)^{\Delta n} \qquad (14.8)$$

In the same way as K_p changes with pressure at high pressures, so will K_x (or K_c) for real solutions change with the concentration of the reagents, i.e. K_x and K_c will no longer be true equilibrium constants. If the chosen standard states differ from those generally adopted, we may use mole fractions as previously, because for the components of an ideal solution at any standard states, a_i remains proportional to x_i.

When calculating equilibrium for real solutions, the activities and standard Gibbs energies must be related to the same standard states.

Example 6. The results of studying the reaction of esterification of pentene with trichloroacetic acid

$$CCl_3COOH(lq) + C_5H_{10}(lq) = CCl_3COOC_5H_{11}(lq)$$

at $t = 100\,°C$ are given below:

Number of moles of pentene per mole of acid in initial mixture, a	2.15	4.12	4.48	6.63	6.80
Number of moles of ester formed, y	0.762	0.814	0.820	0.838	0.839

1. May we consider the system to be an ideal solution?

2. Why does the number of moles of ester formed grow slowly with an increase in the number of moles of pentene?

Solution. 1. By Eq. (14.8)

$$K_a = K_x = \frac{x_{est}}{x_{acid} x_{pent}} = \frac{y \Sigma n_i}{(a - y)(b - y)} \qquad (a)$$

where b is the initial amount of acid (CCl_3COOH).

Introducing into Eq. (a) the values of a, y and $b = 1$, we get the mean value of $K_x \approx 5.86$ for all the experiments. The almost complete independence of the equilibrium constant expressed by the mole fractions of the concentration (the mean deviation is 3.7%) permits us to consider that the system is an ideal solution.

2. In Eq. (a), an increase in a causes Σn_i to grow, and therefore y increases very slowly: a more than three-fold increase of a causes y to grow by only 10%.

14.2.3. Heterogeneous Reactions

Solid Phase-Gas Equilibrium. When the solid phase is a solution, the equilibrium constant is expressed by the activities, and for an ideal solution by the concentrations of its components. If the solid phase is a pure substance and the pressure in the system is high, the activity is calculated by Eq. (6.38); at low pressures it can be taken equal to unity. Gaseous reagents, depending on the pressure, will be represented in the equilibrium constant by their partial fugacities or pressures. Therefore, for instance, if sulphides, oxides, carbonates and crystallohydrates dissociate at a pressure close to atmospheric, Eq. (14.7) may be used for calculating the equilibrium constant, i.e.

$$K_a = K_f = K_p = p^n \tag{14.9}$$

where n is the number of moles of the gaseous reagent (sulphur, oxygen, carbon dioxide and water vapour, respectively).

Experiments show that non-volatile and insoluble condensed phases do not affect equilibrium (if the amount of reacting solid and liquid substances is negligible in comparison with their mass present). In this case, their "acting mass" can be considered constant. A change in the mass of the condensed phases due to the using up of the substances (or their formation) during a reaction, unlike the change in mass of gaseous reagents, does not result in a change in composition and therefore does not violate equilibrium.

Although heterogeneous reactions proceed on the phase interface, and not in the gaseous phase, as was assumed previously, this does not contradict our conclusions, because thermodynamics allows us to assess the results of a process regardless of its mechanism.

When calculating equilibrium for a finely dispersed system, the surface energy of the reagents must be taken into account and the equilibrium constant calculated in accordance with the equation

$$\Delta G = \Delta H - T\Delta S + \Sigma \sigma dA_s$$

i.e. the equilibrium constant and, consequently, the yield of a substance should change with a change in the surface area of the reagents (for greater detail see Sec. 14.3.5).

Example 7. Calculate $(K_a)_{773}$ for the process

$$Ag_2O(c) = 2Ag(c) + \frac{1}{2}O_2(g)$$

if $V^c_{Ag} = 10.3$, $V^c_{Ag_2O} = 32.4$ cm³/mol and $(p_{O_2})_{773} = 388.3$ atm.

Solution. Since the dissociation pressure of Ag_2O is very high, the fugacity of the oxygen differs considerably from its pressure, and the activities of silver and silver oxide from unity. The calculations should be performed according to Eq. (14.1), which here becomes

$$K_a = \frac{a^2_{Ag} f^{\frac{1}{2}}_{O_2}}{a_{Ag_2O}}$$

By Eq. (6.38) we find $a_{Ag} = 1.065$ and $a_{Ag_2O} = 1.219$; from Fig. 40 (p. 192) we have $f_{O_2} = 446$ atm. Consequently, $K_a = 19.6$ (whereas $K_f = \sqrt{446} = 21.1$ and $K_p = \sqrt{p_{O_2}} = 19.7$). The unexpectedly good result of calculations by equations which, strictly speaking, cannot be applied in the given case is due to the mutual compensation of a_{Ag} and a_{Ag_2O}.

Example 8. For the reaction

$$C + CO_2 = 2CO$$

$$\Delta G^\circ = 40\,692 - 13.19T \log T + 6.25 \times 10^{-3} T^2 - 0.58 \times \times 10^{-6} T^3 - 8.19T$$

(1) find the yield of CO at $T = 1200$ K and $p = 1$ atm; (2) determine the possibility of liberating carbon in a hydrogen generator during the reduction period if $t = 600$ °C and $p = 1$, and the partial pressures of the CO_2 and CO in the initial gas equal 0.048 and 0.378 atm, respectively, and 0.228 and 0.198 atm in the reacted gas.

Solution. 1. We use the equation given in the initial conditions to find $\Delta G^\circ_{1200} = -9887$ cal/mol, i.e. by Eq. (13.8) we have $(K_p)_{1200} = = 63.1$.

In the given case, a_C, γ_{CO}, $\gamma_{CO_2} = 1$, i.e. equilibrium should be calculated by Eq. (14.7). Therefore

$$63.1 = \frac{p^2_{CO}}{p_{CO_2}} = \frac{(2y)^2}{1-y}\left(\frac{1}{1+y}\right)^{2-1} = \frac{4y^2}{1-y^2}$$

where y is the number of moles of CO_2 that have reacted by the moment equilibrium sets in. From this equation, we find $y = 0.97$, which corresponds to a yield of CO equal to $2 \times 0.97 \times 100/(1 + + 0.97) = 98.5\%$. Consequently, at $T = 1200$ K an equilibrium

mixture should contain 98.5% of CO and 1.5% of CO_2. Measurements made by various investigators give an average of about 2% of CO_2.

2. For the process

$$2CO = CO_2 + C$$

by Eq. (13.3) we have

$$\Delta G = RT \ln \frac{p_{CO_2}}{p_{CO}^2} - RT \ln K_p$$

where K_p is a quantity that is the reciprocal of the equilibrium constant of the reverse reaction. We find the latter by the equation $\Delta G^\circ = \varphi(T)$; hence we get $\log (K_p)_{873} = 1.01$. Therefore

for the initial mixture

$$\Delta G_{873} = 4.576 \times 873.2 \left(\log \frac{0.048}{0.378^2} - 1.01 \right) = -6010 \text{ cal/mol}$$

and for the reacted gas

$$\Delta G_{873} = 4.576 \times 873.2 \left(\log \frac{0.228}{0.198^2} - 1.01 \right) = -1000 \text{ cal/mol}$$

The results of the calculations show that carbon may be liberated both before and after the reaction.

Liquid Phase-Gas Equilibrium. This case includes everything said in the preceding section. It is only necessary to take account of the possibility of the gases dissolving in the liquid phase, and also of the presence of phase equilibrium.

Example 9. Find the composition of the equilibrium phase for the reaction

$$C_2H_4(g) + H_2O(lq) = C_2H_5OH(aq)$$

at $t = 250\,^\circ C$ and $p = 100$ atm. Take as the standard state of ethanol (eth) its state in a solution with $M = 1$ (in this solution $p_{eth} \approx 4$ mm Hg) and the heat of solution of ethanol in water (w) equal to −2500 cal/mol.

Solution. We shall have three equilibria in the given case: phase equilibrium and chemical equilibria in the liquid and vapour phases.

Let us assume that the process being considered has two stages:

$$C_2H_4(g) + H_2O(lq) = C_2H_5OH(lq) \qquad (1)$$

and

$$C_2H_5OH(lq) = C_2H_5OH(aq) \qquad (2)$$

and calculate ΔG°_{298} for the process as a whole.

According to the data of Table 14, for the first reaction, we have $\Delta G^\circ_{298} = -1271$ cal/mol. We shall assume that the second reaction proceeds as follows: the ethanol isothermally evaporates at the equilibrium pressure (I), the vapour obtained expands to its partial pressure over the solution (II), after which it condenses into the solution (III). Since ΔG° does not depend on the path of the process, we have

$$\Delta G^\circ_2 = \Delta G^\circ_{\mathrm{I}} + \Delta G^\circ_{\mathrm{II}} + \Delta G^\circ_{\mathrm{III}} = 0 + RT \ln \frac{p_{\mathrm{eth}}}{p^\circ_{\mathrm{eth}}} + 0$$

From Fig. 55 $(p^\circ_{\mathrm{eth}})_{298} = 57$ mm Hg. Hence

$$(\Delta G^\circ_{\mathrm{II}})_{298} = 4.576 \times 298.2 \log \frac{4}{57} = -1570 \text{ cal/mol}$$

$$\Delta G^\circ_{298} = -1271 + (-1570) = -2841 \text{ cal/mol}$$

whence

$$\log (K_a)_{298} = -\frac{2841}{4.576 \times 298.2} = 2.082 \quad \text{and} \quad (K_a)_{298} = 121$$

From the data given in Table 1, we have

$$(\Delta H^\circ_1)_{298} = (-66\,190) - [12\,540 - (-68\,315)] = -10\,413 \text{ cal/mol}$$

therefore

$$\Delta H^\circ_{298} = (-10\,413) + (-2500) \approx 12\,900 \text{ cal/mol}$$

Considering in the first approximation that $\Delta H^\circ = \text{const}$, we get in accordance with Eq. (13.12)

$$\log \frac{(K_a)_{523}}{121} = \frac{-12\,900}{4.576} \left(\frac{1}{298.2} - \frac{1}{523.2} \right)$$

whence $\log (K_a)_{523} = -1.984$ and $(K_a)_{523} \approx 0.0104$.

For the given process

$$K_a = \frac{a_{\mathrm{eth}}}{f_{\mathrm{ethene}} a_{\mathrm{w}}}$$

Since the concentration of the ethanol is low, we assume that $a_{\mathrm{eth}} \approx m_{\mathrm{eth}}$ and $a_{\mathrm{w}} \approx x_{\mathrm{w}}$. As a result we get

$$K_a \approx \frac{m_{\mathrm{eth}}}{(f^\circ_{\mathrm{ethene}} x_{\mathrm{ethene}}) x^{\mathrm{lq}}_{\mathrm{w}}}$$

For $\pi = 100/50.0 = 2.00$ and $\tau = 523.2/282.4 = 1.85$ we get $\gamma_{\mathrm{ethene}} = 0.95$ (see Fig. 40, p. 192), i.e. $f^\circ_{\mathrm{ethene}} = 95$ atm. Hence

$$0.0104 = \frac{x^{\mathrm{lq}}_{\mathrm{eth}}}{95 - x^{\mathrm{lq}}_{\mathrm{w}}}$$

Owing to the poor solubility of ethene, we can consider that the liquid phase consists of C_2H_5OH and H_2O. Therefore,

$$0.0104 = \frac{55.55 x_{eth}^{lq}}{95(1 - x_{eth}^{lq})}$$

whence $x_{eth}^{lq} \approx 0.017$.

14.2.4. Electrochemical Reactions

Combination of Eqs. (13.1) and (13.3) yields

$$E = E^\circ - \frac{RT}{zF} \ln \frac{a_R^r a_S^s \dots}{a_B^b a_C^c \dots} \qquad (14.10)$$

where according to Eq. (13.6) the quantities

$$E^\circ = \frac{RT}{zF} \ln K_a \quad \text{or} \quad \Delta G^\circ = -23\,062 z E^\circ \qquad (14.11)$$

correspond to the e.m.f. of a cell when the activity of each of the reagents equals unity.

Since an electrochemical process, for instance

$$\frac{1}{2} Me + H^+(m) = \frac{1}{2} Me^{2+} + \frac{1}{2} H_2$$

is the result of two electrode processes, the e.m.f. is also the difference between two electrode potentials, which are, respectively,

$$E_1 = E_1^\circ - \frac{RT}{F} \ln a_{Me^{2+}} \quad \text{and} \quad E_2 = E_2^\circ - \frac{RT}{F} \ln \frac{\sqrt{p_{H_2}}}{a_{H^+}} \qquad (14.12)$$

where E_1° and E_2° are the standard potentials of the corresponding electrodes.

By relating all the electrodes to a hydrogen one whose standard potential is taken equal to zero, we get the standard electrode potentials ($p = 1$ atm, $t = 25\,°C$) * (Table 24). In accordance with Table 24, every element that is higher in the table displaces ions of a lower element from an aqueous solution (provided that the corresponding activities equal unity).

Knowing the e.m.f., we can determine the activity of the electrolyte by following the principle described in Sec. 12.2. For greater accuracy, the experimental relationship of the e.m.f. is extrapolated to infinite dilution not according to the concentration, but depending on $I^{\frac{1}{2}}$, where I is the ionic strength of the solution (see Sec. 12.2).

* The standard Gibbs energies of ions are calculated by Eq. (14.11) on the basis of the values of the standard electrode potentials.

Table 24. **Standard Electrode Potentials of Selected Cells and Half-Cells** *

Electrode reaction	$-E^{\circ}_{298}$, V
$Li(c) = Li^{+} + e^{-}$	−3.045
$K(c) = K^{+} + e^{-}$	−2.925
$Ca(c) = Ca^{2+} + 2e^{-}$	−2.866
$Na(c) = Na^{+} + e^{-}$	−2.714
$Na(Hg) + Cl^{-}(sat.\ NaCl) = NaCl(c) + e^{-}$	−1.838
$H_2(g) + 2(OH)^{-} = 2H_2O(lq) + 2e^{-}$	−0.828
$Zn(c) = Zn^{2+} + 2e^{-}$	−0.763
$Ga(c) = Ga^{3+} + 3e^{-}$	−0.53
$Fe(c) = Fe^{2+} + 2e^{-}$	−0.440
$Cd(c) = Cd^{2+} + 2e^{-}$	−0.403
$Cr^{2+} = Cr^{3+} + e^{-}$	−0.408
$Tl(c) = Tl^{+} + e^{-}$	−0.336
$Pb(Hg) + 2Cl^{-} = PbCl_2(c) + 2e^{-}$	−0.268
$Ni(c) = Ni^{2+} + 2e^{-}$	−0.250
$Ag(c) + I^{-} = AgI(c) + e^{-}$	−0.152
$Sn(c) = Sn^{2+} + 2e^{-}$	−0.136
$Pb(c) = Pb^{2+} + 2e^{-}$	−0.126
$\frac{1}{2} H_2(g) = H^{+} + e^{-}$	0.000
$Ag(c) + Br^{-} = AgBr(c) + e^{-}$	0.071
$Cu(c) + Cl^{-} = CuCl(c) + e^{-}$	0.137
$2Hg(lq) + 2Br^{-} = Hg_2Br_2(c) + 2e^{-}$	0.140
$Sn^{2+} = Sn^{4+} + 2e^{-}$	0.151
$Ag(c) + Cl^{-} = AgCl(c) + e^{-}$	0.222
$2Hg(lq) + 2Cl^{-} = Hg_2Cl_2(c) + 2e^{-}$	0.268
$Cu(c) = Cu^{2+} + 2e^{-}$	0.337
$4(OH)^{-} = O_2(g) + 2H_2O(lq) + 4e^{-}$	0.401
$I^{-} = \frac{1}{2} I_2(c) + e^{-}$	0.536
$Ag(c) + BrO_3^{2-} = AgBrO_3(c) + e^{-}$	0.55
$2Hg(lq) + SO_4^{2-} = Hg_2SO_4(c) + 2e^{-}$	0.615
$Fe^{2+} = Fe^{3+} + e^{-}$	0.771
$Ag(c) = Ag^{+} + e^{-}$	0.799

* For a complete table see Khomutov, N. E. Table of Standard Electrode Potentials and Their Temperature Coefficients. In: *Itogi nauki. Elektrokhimiya. Elektroosazhdenie metallov i splavov* (Scientific Results. Electrochemistry. Electrodeposition of Metals and Alloys), pp. 7-58 (Vyp. 1). Moscow, VINITI AN SSSR (1966).

Table 24 (concluded)

Electrode reaction	$-E^\circ_{298}$, V
$Hg(lq) = \frac{1}{2}Hg_2^{2+} + e^-$	0.798
$\frac{1}{2}Hg_2^{2+} = Hg^{2+} + e^-$	0.920
$Br^- = \frac{1}{2}Br_2(lq) + e^-$	1.065
$\frac{1}{2}I_2(c) + 3H_2O(lq) = IO_3^- + 6H^+ + 5e^-$	1.195
$2H_2O(lq) = O_2(g) + 4H^+ + 4e^-$	1.225
$Cl^- = \frac{1}{2}Cl_2(g) + e^-$	1.360
$\frac{1}{2}Br_2(lq) + 3H_2O(lq) = BrO_3^- + 6H^+ + 5e^-$	1.491
$Co^{2+} = Co^{3+} + e^-$	1.81
$F^- = \frac{1}{2}F_2(g) + e^-$	2.87

Example 10. At $t = 25\,^\circ C$, the e.m.f. of the cell

$$Cd\,|\,CdCl_2(m)\,\|\,AgCl\,|\,Ag$$

has the following values:

m	0.000 126	0.000 158 5	0.000 199 5	0.000 501 2
E	0.9523	0.9445	0.9365	0.9035

m	0.000 631	0.007 943	0.001
E	0.8954	0.8876	0.8801

Calculate ΔG°_{298} for the reaction proceeding in the cell, the activity coefficient of $CdCl_2$ at $m = 0.0005$ and the standard potential of a cadmium electrode.

Solution. During operation of the cell, the reaction

$$Cd + 2AgCl = CdCl_2 + 2Ag$$

proceeds. By Eq. (14.10) we have

$$E = E^\circ - \frac{RT}{zF}\ln\frac{a_{Cd^{2+}}\,a_C^2 - a_{Ag}^2}{a_{Cd}\,a_{AgCl}^2}$$

or

$$E = E^\circ - \frac{0.059\ 18}{2} \log (\gamma m)(2\gamma m)^2$$

Assuming that $\gamma = 1$ and substituting E°_{cond} for E°, we calculate E°_{cond}, and after constructing a graph in the coordinates E°_{cond} against $\frac{1}{I^2}$, we shall find $E^\circ_{\text{cond}} = E^\circ$ for $I = 0$ ($m = 0$). According to the graph, we have $E^\circ = 0.6215$ V, whence from Eq. (14.11) we get $\Delta G^\circ_{298} = -28\,670$ cal/mol. Inserting the values of E°, $m = 0.0005$ and $E_{m=0.0005}$ into the expression for the e.m.f. of a cell, we find $\gamma = 0.802$.

The standard potential of a cadmium electrode

$$-E^\circ_{\text{Cd}} = 0.222 - 0.6215 = -0.3995 \text{ V}$$

which differs from the most authentic value (see Table 24) by 0.003 V.

Example 11. The standard potential of the electrode Ag, $Ag_2O(c)\,|OH^-$ is 0.344 V. Find the temperature at which the Ag_2O will dissociate in air.

Solution. In the given case

$$E = E^\circ + \frac{RT}{4F} \ln p_{O_2}$$

Since for an oxygen electrode $E^\circ = 0.401$ (see Table 24), we have

$$0.344 = 0.401 + \frac{0.059\ 18}{4} \log p_{O_2}$$

whence $p_{O_2} = 1.41 \times 10^{-4}$.

For the reaction

$$2Ag_2O = 4Ag + O_2$$

we have $\Delta H^\circ_{298} = 14\,880$ cal/mol (see Appendix 2). Considering in the first approximation that $\Delta C_p = 0$, from Eq. (13.11) we get

$$\log (1.41 \times 10^{-4}) = -\frac{14\,880}{4.576 \times 298.2} + B$$

whence $B = 7.05$.

We find the required temperature from the relationship

$$\log 0.21 = -\frac{14\,880}{4.576T} + 7.05$$

We get $T = 420.7$ K or $t = 147.5$ °C (the experimentally found value is approximately 150 °C).

14.3. INFLUENCE OF VARIOUS FACTORS ON THE EXTENT OF A REACTION

Let us rewrite Eq. (14.6) in the form

$$\frac{n_R^r n_S^s \dots}{n_B^b n_C^c \dots} = \frac{K_a}{K_\gamma}\left(\frac{n_B + n_C + \dots + n_R + n_S + \dots + n_{in.g}}{p}\right)^{\Delta n} \quad (14.13)$$

We shall consider the influence of temperature, pressure, the presence of an inert gas, the ratio between the reagents and the degree of dispersity on the yield of the products. Any change in the conditions increasing the right-hand side of Eq. (14.13) obviously also increases the extent of a reaction.

14.3.1. Temperature

An elevation of temperature increases the yield of the products of endothermic reactions. The greater the value of ΔH, the higher is the rate of growth of the equilibrium constant with elevation of temperature and, therefore, of the yield of the products. If a reaction is attended by the liberation of heat, the action of heating will be negative. Therefore, in accordance with **van't Hoff's rule of mobile equilibrium,** which is a special case of the principle of equilibrium displacement, low temperatures favour exothermic reactions (particularly various syntheses), and high temperatures favour endothermic reactions (particularly dissociation). The composition of an equilibrium mixture will change at high pressures, and this will cause K_γ to change with a change in temperature (see Fig. 185).

In accordance with the equation $\Delta G = \Delta H - T\Delta S$, the influence of temperature can also be assessed according to the sign of ΔS: at $\Delta S > 0$ heating favours a process, while at $\Delta S < 0$ the opposite holds. Both criteria (ΔH and ΔS) give identical results, because we are dealing with the influence of temperature on *equilibrium* when $\Delta G = 0$, i.e. the equation $\Delta H = T\Delta S$ holds (while $T \neq 0$). It is also obvious that if the *sign* of ΔS (or ΔH) determines the direction of displacement of equilibrium, then the absolute *value* of ΔS (or ΔH) determines the extent of its displacement. Both these factors are important.

It is often easier to use ΔS for orientation than ΔH, because it is frequently simpler to determine the sign of ΔS than that of ΔH.

In research, equilibrium is studied under almost isothermal conditions; industrial processes are intermediate between *isothermal* and *adiabatic*.

Reactions with low heat effects and with comparatively great heat effects in conditions of good heat exchange are almost isothermal.

Processes in which the heat effects are great and heat exchange is hampered (combustion processes, reactions in tubular apparatus, in apparatus with a contact mass, etc.) are almost adiabatic. Here the extent of a reaction depends on the final temperature. But the value of the latter, in turn, is determined by the heat effect of the reaction. Therefore, unlike an isothermal process, calculation of the yield in this case consists in the simultaneous solution of Eq. (14.13) and an equation relating the extent of a reaction to the value of the final temperature (i.e. a heat balance equation). Graphical solution consists in finding the point of intersection of the curves corresponding to these equations (see the diagram in Fig. 186).

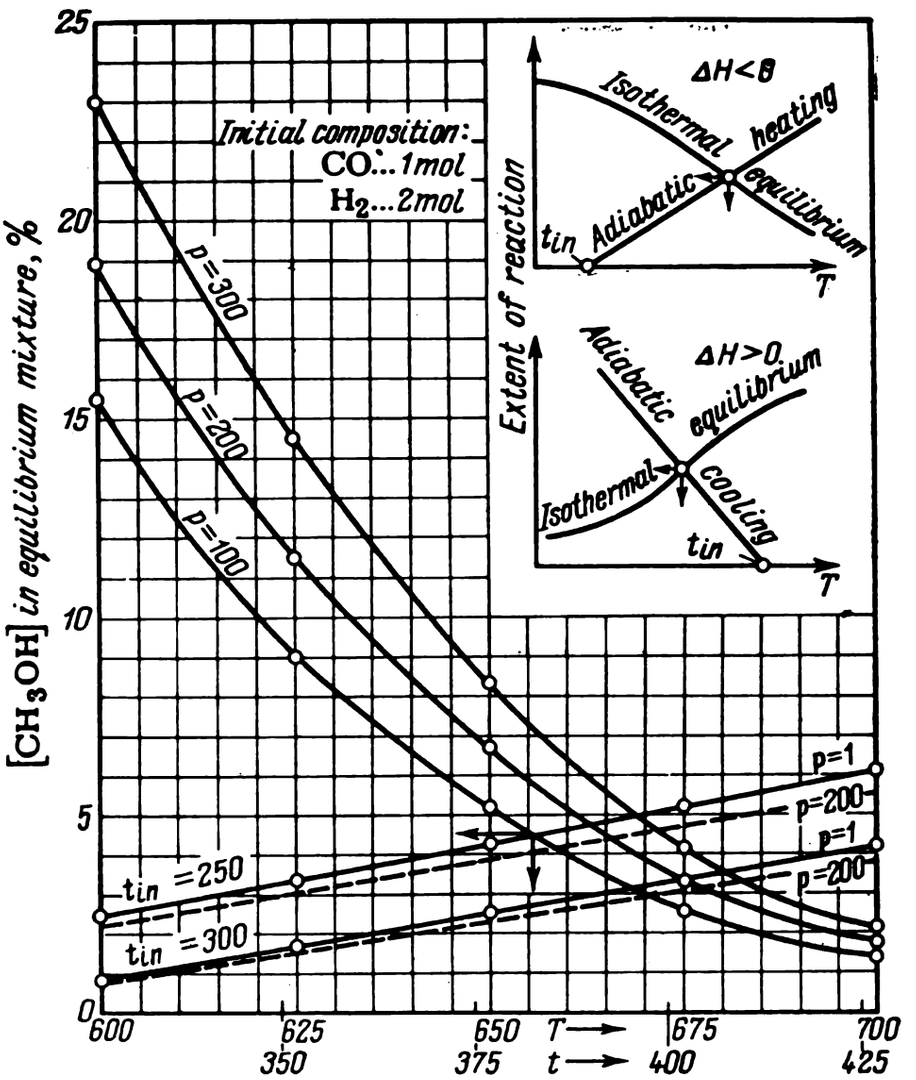

Fig. 186. Influence of temperature and pressure on the extent of the reaction $CO + 2H_2 = CH_3OH(g)$.
(See Example 13)

If a process is exothermic, the equilibrium yield in an adiabatic process is considerably lower than in an isothermal one (the synthesis of methanol, the contact production of SO_2, etc.). In such

cases, it is sometimes good to conduct the process in two stages with intermediate cooling; this allows us to simultaneously use the heat for heating the reactants and regulate the temperature of the process.

Example 12. Answer the following questions on the basis of an analysis of the equation $\Delta G^\circ = \varphi(T)$ given in the initial conditions of Example 8 (p. 534) for the reaction

$$C + CO_2 = 2CO$$

1. What is the composition of the gas mixture at temperatures below 400 and above 1000 °C?
2. How can we explain the deposition of carbon black on the walls upon the cooling of gases passing through chambers or flues?
3. How does the reducing power of the gaseous phase change with elevation of the temperature?
4. Why is the temperature of burning coal higher when air is blown in rapidly than when it is supplied at a slow rate?

Solution. The solution follows from the Le Chatelier principle and is due to the endothermic nature of the process of reducing CO_2.

1. Below 400 °C, an equilibrium mixture consists almost completely of CO_2. Indeed, from the equation $\Delta G^\circ = \varphi(T)$, we find $\Delta G^\circ_{673} = 12\,720$ cal/mol, whence $\log (K_p)_{673} = -4.13$, which corresponds to about 0.8% of CO. At elevated temperatures (above 1000 °C) (see the solution of Example 8), on the contrary, the mixture contains almost no CO_2.

2. Upon cooling, equilibrium shifts to the left, and this explains the deposition of carbon on the walls of the apparatus. Therefore, to prevent the deposition of carbon in a hydrogen generator, we have to elevate the temperature (see Example 8). The deposition of carbon should be avoided because of the growth in the consumption of the raw material and pollution of the hydrogen, and also because of the possibility of a drop in the activity of the reaction mixture and the appearance or acceleration of undesirable reactions.

In the conditions of higher temperatures, ΔG grows, but for each temperature we have $\Delta G_{pr} > \Delta G_r$. At known temperatures (about 700 °C for the reaction mixture and 620 °C for the product gas), the system becomes equilibrium; at higher temperatures, no deposition of carbon should be observed.

The process should therefore be conducted at $t > 700$ °C. In addition, the water gas should be heated before it is admitted into the reaction chamber (to prevent contact of the cold gas with the reaction mixture).

3. The reducing power grows with increasing temperature, because equilibrium shifts toward the formation of carbon monoxide.

4. When air is blown in intensively, the CO_2 formed in the oxidation of the coal does not have time to become reduced to CO, i.e. an endothermic reaction whose adiabatic course results in lowering of the temperature does not occur.

Example 13. Use the data given in Example 4 (p. 529) to find the yield of methanol from a stoichiometric mixture of CO and H_2 in conditions of complete thermal insulation of the converter if the gas is supplied at $t = 250\,°C$ and $p = 100$ atm. The temperature dependences of the heat capacities of the reagents are expressed by the following equations:

$$(C_p)_{CO} = 6.60 + 1.20 \times 10^{-3} T,$$

$$(C_p)_{H_2} = 6.62 + 0.81 \times 10^{-3} T,$$

$$(C_p)^g_{CH_3OH} = 2.0 + 30 \times 10^{-3} T$$

Solution. Assuming that the enthalpy of the initial gas mixture at $t = 250\,°C$ equals zero, we compile the equation of the heat balance:

$$-23\,050y + (1 - y)\int_{523.2}^{T} (6.60 + 1.20 \times 10^{-3} T)\, dT +$$

$$+ (2 - 2y)\int_{523.2}^{T} (6.62 + 0.81 \times 10^{-3} T)\, dT +$$

$$+ y\int_{523.2}^{T} (2.0 + 30 \times 10^{-3} T)\, dT = 0$$

where y = number of moles of CH_3OH in the equilibrium mixture

$-23\,230$ = heat effect of the reaction at 250 °C.

We find from this equation that

$$y = \frac{-1.41 \times 10^{-3} T^2 - 19.96T + 10\,829}{13.59 \times 10^{-3} T^2 - 17.96T - 17\,573} \qquad \text{(a)}$$

At the same time in accordance with the solution of Example 4, we have

$$\frac{y(3 - 2y)^2}{4(1 - y)^3} = \frac{K_a}{K_\gamma} \times 1000^2 \qquad \text{(b)}$$

By assigning different values to T, we calculate y from Eqs. (a) and (b) [we determine K_a from the equation $\Delta G^\circ = \varphi(T)$ given in the initial conditions of the above example, and K_γ on the basis of Fig. 40, p. 192]. Calculating the value of y corresponding to an equilibrium content of CH_3OH in per cent, we get:

T, K	600	625	650	675	700
$[CH_3OH]$, %:					
by Eq. (a)	2.47	3.33	4.22	5.17	6.10
by Eq. (b)	15.49	9.01	5.20	2.53	1.39

We plot these data on a graph (see Fig. 186). The intersection of the plotted curves gives the required result: 4.5% of CH_3OH and 383 °C (the final temperature of the process). Thus, the adiabatic nature of the process results in diminishing of the yield to less than one-twelfth of that obtained in isothermal conducting of the reaction (see the solution of Example 4).

Similar calculations can be performed for other conditions. Figure 186 gives the results of calculations for the initial temperature of 300 °C and for pressures of 200 and 300 atm. The dashed line shows the results of approximate calculations with account taken (in the heat balance) of the influence of the pressure on the enthalpy of the reagents (see Fig. 42, p. 195). The change in the yield of methanol and the temperature in the reaction zone is due to a different change in H_t with pressure. At temperatures far from critical, the influence of the pressure may be disregarded.

If calculations must be performed for conditions of a given heat exchange, the losses of heat have to be taken into account in Eq. (a). Here with a constant position of the curves $y_{(b)} = \varphi(T)$, the lines $y_{(a)} = \varphi(T)$ will rise; the temperature in the reaction zone will therefore drop, and the extent of the reaction will grow.

14.3.2. Pressure

The nature of the influence of pressure on the equilibrium yield in accordance with Eq. (14.13) is determined by the sign of the difference Δn between the number of moles of the gaseous reagents and also by the pressure dependence of K_γ.

If the absolute value of Δn is great, the first factor is of decisive significance; when $\Delta n > 0$, an increase in pressure unfavourably affects the yield, and when $\Delta n < 0$, its influence is favourable. For example when acetylene burns in oxygen, it is good to increase the pressure of the gases entering into the reaction: the process is attended by diminishing of the volume, and compression suppresses the dissociation of the combustion products. Another example is cracking. Here an increase in pressure results in a lowering of the yield of the gaseous products, including unsaturated hydrocarbons

combining with hydrogen. When $\Delta n = 0$, the influence of pressure on equilibrium is determined only by the pressure dependence of K_γ. It has not been found possible to establish this relationship in the general form. It should be considered quite definite, however, that the influence of pressure on K_γ is appreciable only at high pressures when the difference between the compressibility of different gases becomes more considerable.

When $\Delta n = 0$, a change in pressure displaces equilibrium. But this is a seeming contradiction of the Le Chatelier principle, because the influence of pressure is determined by the sign of the change in volume. For low pressures, the signs of ΔV and Δn coincide, while for high pressures, $\Delta V \neq 0$, although $\Delta n = 0$ (we also have to take this possibility into consideration when the absolute value of Δn is not great). For instance if for the reaction

$$CO_2 + H_2 = CO + H_2O(g)$$

at $T = 900$ K, we have

$$(K_\gamma)_{p=1} = \frac{\gamma_{CO}\gamma_{H_2O}}{\gamma_{CO_2}\gamma_{H_2}} = \frac{1 \times 1}{1 \times 1} = 1$$

then

$$(K_\gamma)_{p=500} = \frac{1.26 \times 0.76}{1.15 \times 1.12} = 0.74$$

i.e. the equilibrium of the reaction is displaced toward the formation of CO and $H_2O(g)$ [displacement as a result of condensation of the vapour is excluded, because $(T_{cr})_{H_2O} < 900$ K].

The influence of pressure on equilibrium can also be illustrated by the example of the synthesis of ammonia and methanol, where $\Delta n < 0$ and $K_\gamma \neq 1$. We can consider that $K_\gamma = \text{const}$ for the reaction of synthesis of methanol only up to $p \approx 20$ atm. At high pressures, this quantity begins to diminish owing to the great compressibility of methanol and the almost complete coincidence of f_{CO} and f_{H_2} (see Fig. 185). Thus, the increase in the yield of CH_3OH with a growth in pressure is here due to both factors.

A similar phenomenon occurs in the synthesis of ammonia, when the increase in the yields at high pressures with a reduction in the amount of the reagents is due to the greater drop in f_{NH_3} in comparison with the drop in f_{H_2} and f_{N_2}. This is why K_p grows with pressure; the ratio $p_i : p$ for NH_3 grows to a greater extent than for N_2 and H_2, i.e. the content of NH_3 in the equilibrium mixture grows more rapidly than follows from Eq. (14.7). The understated yield of NH_3 obtained by this equation is apparently explained by the fact that molecules of NH_3, unlike those of N_2 and H_2, are dipoles, and as a result ammonia has a greater compressibility than nitrogen and hydrogen.

The influence of pressure on γ_i sometimes also has to be taken into account at not very significant pressures, especially if a reaction proceeds without a change in volume (for example a reaction of isomerization). In this case, the yield may be changed by a slight change in pressure.

Calculations of such an equilibrium must be performed more carefully than for cases when $\Delta n \neq 0$, where by an insignificant change in pressure it is easy to displace equilibrium in the desired direction and thus "correct" the calculations. For example, if an error in the value of the equilibrium constant of 100% was made when calculating the synthesis of ethanol from C_2H_4 and $H_2O(g)$, the transition to the true value will correspond to a change in pressure from 1 to 2 atm.

Example 14. Determine the possibility of preparing diamonds (di) from graphite (gr) if

$$V_C^{gr} = 5.303\,22 + 31.453\times10^{-6}T + 2.001\,90\times10^{-8}T^2 - 16.15\times10^{-6}p$$

$$V_C^{di} = 3.418\,12 - 6.2146\times10^{-6}T + 2.325\,17\times10^{-8}T^2 + 14.958\times10^{-12}T^3 - 0.55\times10^{-6}p$$

Assume that for the reaction $C_{(gr)} = C_{(di)}$

$$\Delta G^\circ = 541.77 + 1.176\,22T\log T - 2.21\times10^{-3}T^2 + 6700T^{-1} - 2.437\,23T$$

Perform the calculations for $T = 298$ to 1400 K and $p = 1$ to 20 000 atm.

Solution. It follows from the latter equation that a growth in T does not favour the preparation of diamonds ($\Delta S < 0$!). This process can be carried out only at a high pressure, because on one hand $(\partial\Delta G/\partial p)_T = \Delta V$ and on the other $\Delta V < 0$. At the same time, since the absolute value of ΔV is extremely low, a very high pressure has to be applied to change the sign of ΔG. This is confirmed by the following calculations:

$$\Delta V = -1.8851 - 37.6676\times10^{-6}T + 0.323\,27\times10^{-8}T^2 + 14.958\times10^{-12}T^3 + 15.6\times10^{-6}p$$

$$\left(\frac{\partial\Delta G}{\partial p}\right)_T = \frac{\Delta V}{41.293} = -0.045\,660 - 0.912\,36\times10^{-6}T + 0.007\,830\times10^{-8}T^2 + 0.3623\times10^{-12}T^3 + 0.38\times10^{-6}p$$

Integration yields

$$\Delta G_{p,T} = \Delta G_{p=1,T} - (0.045\,660 + 0.912\,36\times 10^{-6}T - \\ - 0.007\,830\times 10^{-8}T^2 - 0.3623\times 10^{-12}T^3)(p-1) + \\ + 0.19\times 10^{-6}(p^2-1)$$

or in combination with the equation $\Delta G^\circ = \varphi(T)$

$$\Delta G = 541.82 + 6700T^{-1} + 1.176\,22T\log T - 2.437\,23T - \\ - 2.21\times 10^{-3}T^2 - (0.045\,660 + 0.912\,36\times 10^{-6}T - \\ - 0.7830\times 10^{-10}T^2 - 0.3623\times 10^{-12}T^3)p + 0.19\times 10^{-6}p^2$$

We use this equation to calculate the values of $\Delta G = \varphi(p, T)$. The results of the calculations are plotted in Fig. 187. Taking into account the errors in ΔG° and the considerable error in extrapolating the equation $\Delta G = \varphi(T, p)$ and especially $C_p = \varphi(T)$ to very high pressures, we can nevertheless say with certainty that artificial diamonds can be prepared in principle at pressures of the order of magnitude of 20 000 atm. To achieve acceptable rates, the temperature has to be raised. This requires an increase in the pressure up to from 25 000 to 30 000 atm. At present, industrial diamonds are successfully synthesized at high pressures.

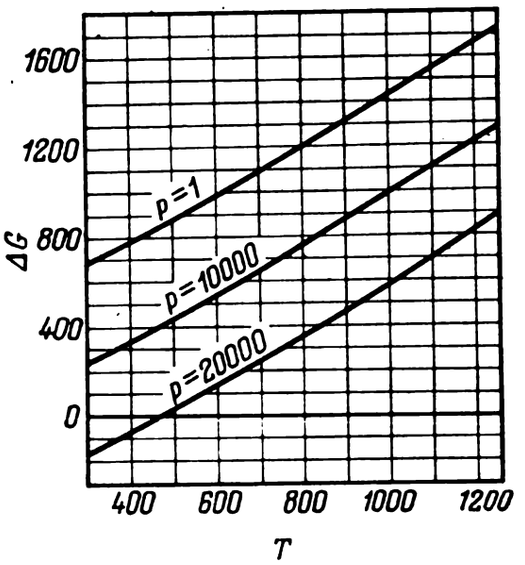

Fig. 187. Dependence of change in the Gibbs energy of the reaction C (graphite) = C (diamond) on temperature and pressure.
(See Example 14)

14.3.3. Presence of an Inert Gas

Let us consider the influence of an inert gas at p = const. The effect of dilution is similar to that of diminishing the total pressure, which can be seen from Eq. (14.13). For instance, if a nitrogen-hydrogen-ammonia mixture taken at $p = 1000$ atm contained 10% of an inert gas, the action of the latter would be equivalent to lowering of the pressure by 250 atm. The gradual accumulation of inert gases (Ar, CH_4, etc.) in this mixture results in a decrease in the ammonia yield, therefore "scavenging" is regularly conducted in industrial installations with the addition of fresh gas.

Consequently, for reactions proceeding with a reduction in volume, dilution with an inert gas is not desirable; conversely,

when the volume grows, dilution with an inert gas increases the theoretical extent of the reaction.

Example 15. How will the yield of NH_3 change in the reaction

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$$

if for $t = 475\,°C$ and $p = 300$ atm we have $K_a = 0.005\,04$ and $K_\gamma = 0.76$? The initial mixture contains 18% of N_2, 72% of H_2 and 10% of inert gases; when using a stoichiometric mixture, we get 31% of NH_3.

Solution. In accordance with Eq. (14.6), we have

$$0.005\,04 = \frac{y}{(0.18 - 0.5y)^{\frac{1}{2}}(0.72 - 1.5y)^{\frac{3}{2}}} 0.76 \left(\frac{300}{1-y}\right)^{1-2}$$

or

$$\frac{y(1-y)}{(0.18 - 0.5y)^{\frac{1}{2}}(0.72 - 1.5y)^{\frac{3}{2}}} = 1.99$$

whence by the method of consecutive approximation we find $y = 0.20$ or $\frac{0.20}{1 - 0.20} \times 100 = 25\%$ of NH_3. Consequently, the yield of ammonia drops by almost 20%.

14.3.4. Ratio of Reagents

A stoichiometric mixture of the reactants is needed to obtain the *maximum yield* of the products .* An excess amount of the reactants is needed to achieve the *maximum extent of a reaction* (*degree of transformation*). Therefore, if the available amount of one of them is limited for technological or economical reasons, an increase in the initial concentration of the other reactants will increase the number of moles of products formed and thus raise the extent of the reaction. Here we must take into account the ease with which the unreacted excess amount of the reactants from the resulting mixture can be removed.

The extent of a reaction can also be increased by removing the products from the reaction zone, binding them in poorly dissociating, poorly soluble or non-volatile substances. Such a method is quite rational because there is no need to have a large surplus of a reactant. Thus, if in the conversion of CO it is possible in some way

* This is easy to prove by investigating Eq. (14.13) for a maximum with respect to the yield of the product. See, for example, [A10].

or other to lower the concentration of CO_2 without changing the partial pressure of the water vapour supplied to the converter, the pressure of the CO will also diminish and the mixture will become richer in hydrogen.

The presence of the products in the initial mixture results in a lowering of the extent of a reaction.

Example 16. What amount of CO_2 has to be added to water gas to prevent the deposition of carbon without changing the temperature conditions in the hydrogen generator (see Example 8, p. 534).

Solution. Denoting by y the number of moles of CO_2 added to one mole of the water gas, in accordance with Eq. (14.7) and Fig. 163 (p. 443) we get for $t = 600\,°C$

$$\frac{0.048 + y}{0.378^2}\left(\frac{1}{1+y}\right)^{1-2} \geqslant 10.28$$

whence $y \geqslant 0.778$. Although with increasing temperature, the equilibrium constant of the reaction $2CO = C + CO_2$ diminishes resulting in a smaller amount of additional CO_2 being needed (at $t = 650\,°C$ we have $y \geqslant 0.414$; conversely, at $t = 500\,°C$ we have $y \geqslant 2.00$), the required excess amount of CO_2 is very great. Consequently it is more expedient to raise the temperature, all the more since this favours three of the four basic reactions proceeding in the production of hydrogen by the iron and steam process: the reaction of CO with FeO, of H_2 with FeO and of H_2 with Fe_3O_4 (see Fig. 163).

Instead of a surplus of CO_2, it would have been possible to introduce a surplus of $H_2O(g)$ or use partly burned water gas for reduction, because the ratio $[CO] : [CO_2]$ can also be lowered in this way.

14.3.5. Change in Surface Area

V. Kireev (1951) showed that a change in the degree of dispersity and compactness of phases may appreciably affect the chemical activity of a substance. Therefore, when calculating the equilibrium of reactions in which finely crystalline, amorphous and vitreous substances participate, we must take into account the additional change in the Gibbs energy $dG_s = \Sigma d(\sigma_i A_{s_i})$, and equilibrium will correspond to the condition

$$dG + dG_s = 0$$

where dG is the change in the Gibbs energy without taking into consideration the above factor.

Since we can consider the surface tension to be constant in the course of a reaction (we exclude the possibility of its changing when

the size of the particles changes), the change in the Gibbs energy due to a change in the magnitude of all the interfaces will be

$$\Delta G_s = \Sigma \sigma_i \Delta A_{s_i} = \Delta H_s - T\Delta S_s = RT \ln \frac{K_a}{K'_a} \qquad (14.14)$$

where ΔH_s and ΔS_s = changes in enthalpy and entropy of a unit of surface area related to one mole of a given phase (they can be found by calorimetric measurements)

K'_a = value of the equilibrium constant taking into account the influence of the surface energy.

For example for the reaction

$$MeCO_3 = MeO + CO_2$$

proceeding in a highly dispersed system, we have

$$\Delta G_s = RT \ln \frac{p_{CO_2}}{p'_{CO_2}}$$

If the carbonate is comminuted, the pressure of dissociation will grow (because $dA_s < 0$ for $MeCO_3$, and $dG_s > 0$). If MeO is in the dispersed state, then p'_{CO_2} will be less than p_{CO_2}.

The following data can show the magnitude of such effects. Upon the transition from the crystalline to the vitreous (glassy) state, the Gibbs energy grows by 2700 for SiO_2 and by 2600 cal/mol for B_2O_3. The transition of graphite into amorphous carbon with a density of 1.86 g/cm³ is attended by the absorption of 3640 cal/g-atom. These values, in accordance with Eq. (14.14), correspond to an increase in the equilibrium constant of scores of times.

The quantities ΔG_s may reach values exceeding the change in the Gibbs energy upon the transition from one crystalline modification to another.

In accurate calculations, account must also be taken of the difference between G for large crystals and minerals, which because of their more compact structure have a lower absolute entropy and a greater entropy and energy of formation. We sometimes have to take into consideration the fact that different forms of minerals differ in their properties: for instance chalk has a less compact structure than marble, while the latter, in turn, has different properties depending on the density (for example if one mole of marble whose density equals 2.714 g/cm³ were to transform into marble with a density of 2.884 g/cm³, 141 calories of heat would be liberated); the transition of amorphous carbon having a density of 2.07 g/cm³ to amorphous carbon with a density of 1.86 g/cm³ is attended by the absorption of 1170 calories.

Finally, account must also be taken of the conditions of formation of the crystals (of a given size); the more the lattice is distorted in the process of formation, the higher is the pressure of dissociation.

14.3.6. Kind of Reaction

At identical values of ΔG°_T and identical pressures and ratios of the reagents, the equilibrium yield depends on the ratio between the number of moles of the reactants and products in the stoichiometric equation; the greater the difference in the number of moles of gaseous substances Δn, the greater will be the amount of product obtained.

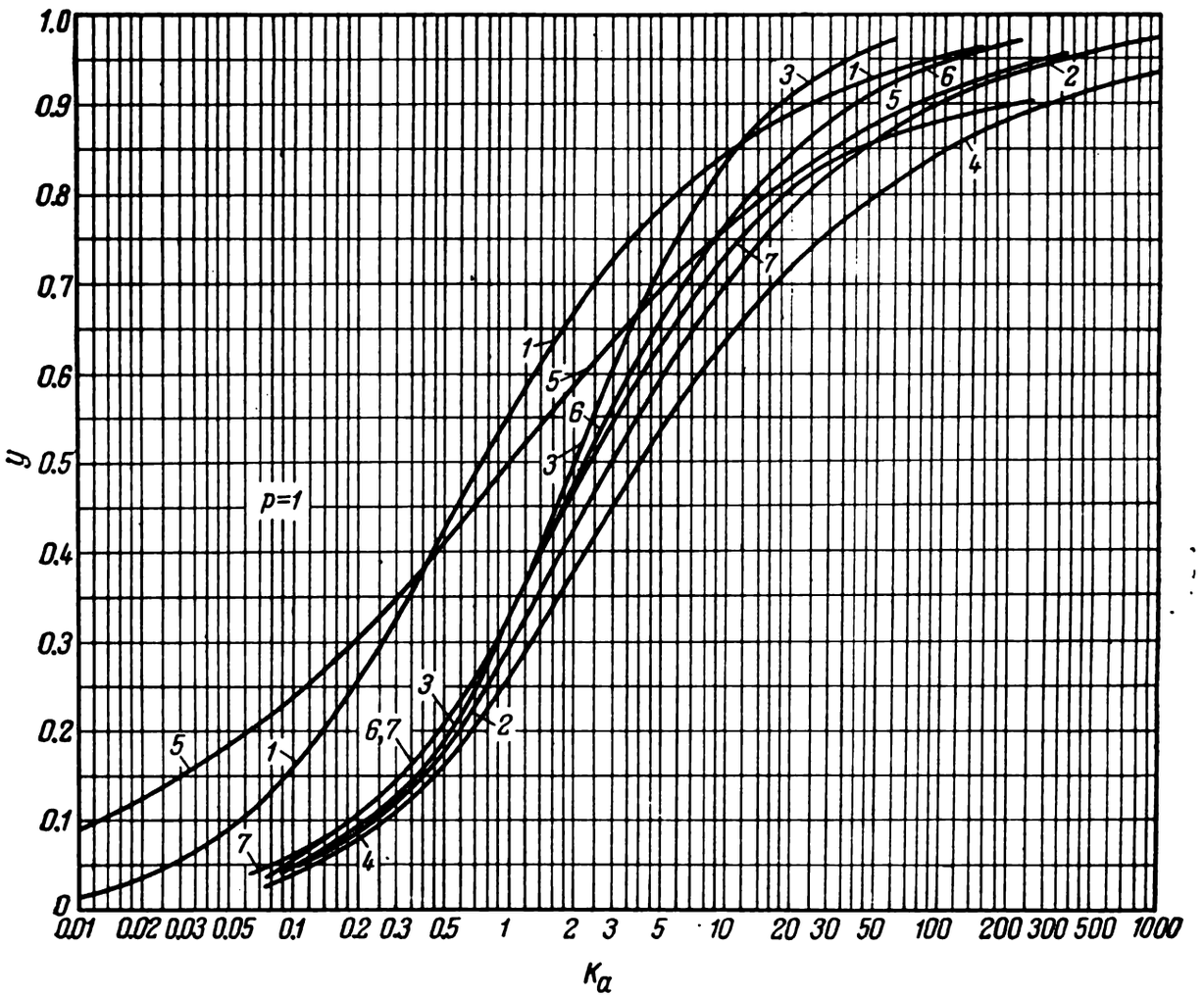

Fig. 188. Relationship between yield and equilibrium constant for various kinds of reactions

Figure 188 shows the relationship between the yield and K_a (K_p) for the following kinds of gaseous reactions at the stoichiometric ratio of the reagents and $p = 1$ atm:

$$1.\ 2B = R \ldots\ldots K_p = \frac{y(2-y)}{p(2-2y)^2}$$

2. $B + C = R$ . . . . $K_p = \dfrac{y(2-y)}{p(1-y)^2}$

3. $\frac{1}{2}B + \frac{1}{2}C = R$ . . $K_p = \dfrac{y}{0.5 - 0.5y}$

4. $B + 2C = R$ . . . . $K_p = \dfrac{y(3-2y)^2}{p^2(1-y)(2-2y)^2}$

5. $B + C = R + S$ . . $K_p = \dfrac{y^2}{(1-y)^2}$

6. $B + \frac{1}{2}C = R$ . . . $K_p = \dfrac{y\sqrt{p(1.5-1.5y)}}{(1-y)\sqrt{0.5-0.5y}}$

7. $\frac{1}{2}B + \frac{3}{2}C = R$ . . $K_p = \dfrac{y(2-y)}{p(1.5-1.5y)^{1.5}\sqrt{0.5-0.5y}}$

Examination of Fig. 188 shows that we cannot assess the equilibrium yield only according to the value of ΔG° or K_p. It must be remembered here that a change in pressure affects the yield differently and displaces equilibrium to a different extent when Δn has the same sign (+ or —).

14.4. EQUILIBRIUM IN COMPLEX CHEMICAL SYSTEMS

When calculating equilibrium concentrations, account must always be taken of the possibility of side reactions that may cause displacement of equilibrium. Here additional complications may occur. For example, if in the synthesis of NH_3 or SO_3 the temperature affects only one reaction, in the synthesis of CH_3OH it also affects the side reactions whose intensity changes with a change in the temperature.

The problem of the technical possibility of a given process can be solved only by taking into consideration the side reactions (see also p. 520 and Sec. 4.6).

The principle of calculating equilibrium in complex systems consists in the following. Knowing the initial composition of the system, we can express its equilibrium composition and write down the expression for the equilibrium constant for each of the reactions. The activities of all the substances at the moment of equilibrium must satisfy all the equations of equilibrium for any reaction possible in the system. In other words, the activity (in practice the concentration or partial pressure) of each reagent for all the reactions occurring in the given system should have the same value. Other-

wise there would be no equilibrium. We determine the equilibrium composition of the system by solving the system of equations obtained relative to all the unknown quantities (this is usually done by the method of successive approximations).

Only independent reactions must be taken into consideration in the calculations. Their number equals the number of all the substances in the system minus the sum of unlike atoms which the reagents are formed from. Hence the number of equations to be solved diminishes.

The calculations can be simplified by making a number of assumptions. For example, we can ignore all reactions for which K_a is either very great or very small. In the first case, the ignored reactions proceed practically to the end, in the second, they hardly proceed at all. Thus, the following processes are possible in reducing sulphur dioxide with air-producer gas:

$$2CO + SO_2 = 2CO_2 + \frac{1}{2} S_2(g)$$

$$CO + \frac{1}{2} S_2(g) = COS$$

$$2COS = CO_2 + CS_2$$

Within the interval from 350 to 1000 °C, however, the carbon disulphide is present in the system in very insignificant amounts (its partial pressure at $p = 1$ atm fluctuates from 3×10^{-6} to 2×10^{-5} atm); consequently, the last reaction may not be taken into account.

Other ways of simplification are also possible. For instance, in calculating isomerization processes, the equilibrium mixture can be considered an ideal solution.

When a reaction proceeds in several stages, the value of the equilibrium constant may not correspond to the equilibrium yield of the products, because it equals the corresponding product of the values of the equilibrium constants for the intermediate reactions. If the equilibrium constants of the intermediate, particularly of two, reactions are incommensurable, then depending on whether $(K_a)_1$ or $(K_a)_2$ is greater, either intermediates $[(K_a)_1 \gg (K_a)_2]$ or products $[(K_a)_2 \gg (K_a)_1]$ should predominate in the equilibrium mixture. We can therefore ignore the corresponding reaction (reactions). Consequently, a high value of the equilibrium constant for a total reaction does not always correspond to a considerable yield of the product we are interested in. For this reason, the equation of the equilibrium constants for the total reaction is only useful for calcu-

lating the composition of an equilibrium mixture when there are few intermediates. If the equilibrium constants are commensurable, we cannot disregard any reaction, and the equilibrium mixture may contain products of side and the main reactions. The rate acquires special significance for the actual carrying out of a process, because by using selective catalysts we often succeed in achieving such a ratio between the rates of the possible reactions that ensures the desired effect. In this case, the actual equilibrium is not calculated, because only a part of the proceeding reactions is considered. In the long run, true equilibrium corresponding to all the conceivable processes will set in in such a system. Owing to the limited time in which the reaction proceeds, however, we may take only the relatively rapid reactions into consideration in practical conditions.

Example 17. The reaction

$$\frac{1}{2}N_2 + CO_2 = CO + NO$$

was proposed to prepare bound nitrogen. If we perform the calculations for $T \approx 3000\text{-}3500$ K (the temperature of a voltaic arc), ignoring the possibility of other reactions, the yield will be about 10%. At the same time, the maximum yield in experiments is 3%. Explain the discrepancy between the results and confirm the experimental data by calculations.

Solution. Regardless of the results of checking, we cannot ignore side reactions: at such high temperatures, the process of binding nitrogen with the aid of carbon dioxide should be attended by the dissociation of NO and CO_2 (the inhibition of equilibrium at such high temperatures is excluded). We must therefore simultaneously consider three reactions:

$$\frac{1}{2}N_2 + CO_2 = CO + NO \quad (1)$$

$$CO_2 = CO + \frac{1}{2}O_2 \quad (2)$$

$$NO = \frac{1}{2}N_2 + \frac{1}{2}O_2 \quad (3)$$

Proceeding from a stoichiometric mixture of N_2 and CO_2 and considering that at the moment of equilibrium we have $n_{CO} = x$, $n_{NO} = y$ and $n_{O_2} = z$, we get the equilibrium content of the other components: $n_{CO_2} = 1 - x$ and $n_{N_2} = 0.5 - 0.5y$, while the total

number of moles $\Sigma n_i = 1.5 + 0.5y + z$. Hence at $p = 1$ atm, in accordance with Eq. (14.7), we have

$$(K_p)_1 = \frac{p_{NO} p_{CO}}{p_{N_2}^{\frac{1}{2}} p_{CO_2}} = \frac{xy}{(0.5 - 0.5y)^{\frac{1}{2}} (1 - x)} \left(\frac{1}{1.5 + 0.5y + z} \right)^{\frac{1}{2}} \quad \text{(a)}$$

$$(K_p)_2 = \frac{p_{CO} p_{O_2}^{\frac{1}{2}}}{p_{CO_2}} = \frac{xz^{\frac{1}{2}}}{1 - x} \left(\frac{1}{1.5 + 0.5y + z} \right)^{\frac{1}{2}} \quad \text{(b)}$$

$$(K_p)_3 = \frac{p_{N_2}^{\frac{1}{2}} p_{O_2}^{\frac{1}{2}}}{p_{NO}} = \frac{(0.5 - 0.5y)^{\frac{1}{2}} z^{\frac{1}{2}}}{y} \quad \text{(c)}$$

Of the three reactions, only two are independent (five kinds of molecules are formed from three atoms); therefore, for example, $(K_p)_1 = (K_p)_2/(K_p)_3$. Hence, another equation is needed. We shall find it by compiling a material balance with respect to oxygen: 1 (in 1 mol of CO_2) $= 0.5x$ (in x mol of CO) $+ 0.5y$ (in y mol of NO) $+ z$ (in z mol of O_2) $+ (1 - x)$ [in $(1 - x)$ mol of CO_2] whence $z = 0.5x - 0.5y$.

Excluding the quantity z from Eqs. (b) and (c), we get

$$(K_p)_2 = \frac{x(0.5x - 0.5y)^{\frac{1}{2}}}{(1.5 + 0.5x)^{\frac{1}{2}} (1 - x)} \quad \text{(b')}$$

$$(K_p)_3 = \frac{(0.5 - 0.5y)^{\frac{1}{2}} (0.5x - 0.5y)^{\frac{1}{2}}}{y} \quad \text{(c')}$$

We find the values of $(K_p)_2$ and $(K_p)_3$ from equations $\Delta G^\circ = \varphi(T)$ for the reactions being considered. To find x and y and thus determine the equilibrium composition, we shall assume a probable value of y (or x). Introducing it into Eq. (b'), we calculate x, then insert the values of x and y in Eq. (c'). We get a quantity that will differ somewhat from the value of $(K_p)_3$ found by the equation $\Delta G^\circ = \varphi(T)$. By plotting these results on a graph and repeating such calculations several times, we get a number of points through which we draw a curve. Next by interpolation, we determine the required value of y corresponding to the value of $(K_p)_3$ for a given temperature (Fig. 189). This method is especially convenient when it is necessary to determine the equilibrium composition for a number of temperatures. It would be possible to plot the values of x

found from Eqs. (b') and (c') against the adopted values of y. The intersection of the curves found in this way would also give the required result.

According to calculations, the yield of NO in an equilibrium mixture at $T = 3000$ K is 1.4%, at 3500 K it is 3.5%, whereas according to experimental data the yield of NO at 3000 to 3500 K ranges from 1.38 to 3.05%. Calculations without taking dissociation into account give 7.6 and 18.0%, respectively.

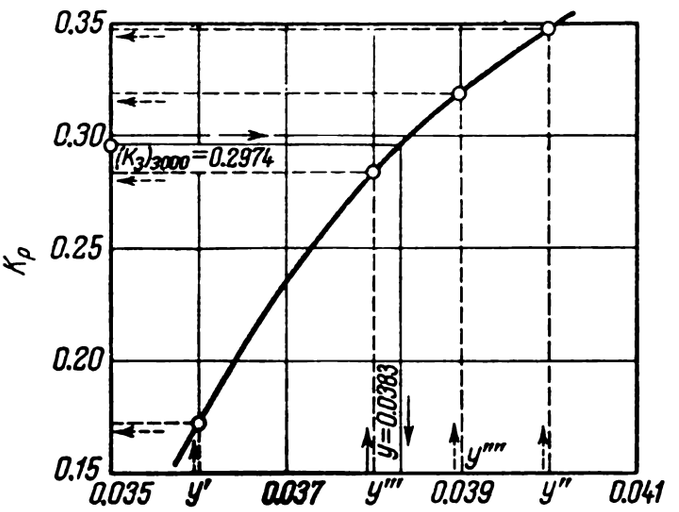

Fig. 189. Calculating the composition of an equilibrium mixture by the method of successive approximations (y', y'', etc. are the assumed number of moles of NO at the moment of equilibrium).
(See Example 17)

Example 18. Calculate the conversion of methane with steam, if (1) $[CH_4] : [H_2O] = 1 : 2$, and (2) $[CH_4] : [H_2O] = 1 : 4$. Perform the calculations for the interval from 500 to 1200 °C ($p = 1$ atm).

Solution. In the conversion of CH_4 with H_2O, the reaction mixture will contain CH_4, H_2O, CO, CO_2 and H_2, because the following reactions proceed simultaneously:

$$CH_4 + H_2O(g) = CO + 3H_2 \quad (1)$$

$$CO + H_2O(g) = CO_2 + H_2 \quad (2)$$

$$CH_4 + 2H_2O(g) = CO_2 + 4H_2 \quad (3)$$

Only two of these reactions will be independent, and we choose (1) and (2). (The reactions

$$2CH_4 = C_2H_6 + H_2$$

$$H_2O = H_2 + \frac{1}{2}O_2$$

$$CO_2 = CO + \frac{1}{2}O_2$$

may not be considered, because the equilibrium constants for them become significant only at very high temperatures.)

Denoting by n_{CH_4}, n_{H_2O}, n_{CO}, etc. the number of moles of the reactants, by x the number of moles of CH_4 that have reacted accord-

ing to Eq. (1), and by y the number of moles of CO that have reacted according to Eq. (2), we get

$$(K_p)_1 = \frac{p_{CO}p_{H_2}^3}{p_{CH_4}p_{H_2O}} = \frac{(n_{CO} + x - y)(n_{H_2} + 3x + y)^3}{(n_{CH_4} - x)(n_{H_2O} - x - y)} \left(\frac{1}{\Sigma n_i + 2x - y}\right)^2 \quad \text{(a)}$$

and

$$(K_p)_2 = \frac{p_{CO_2}p_{H_2}}{p_{CO}p_{H_2O}} = \frac{(n_{CO_2} + y)(n_{H_2} + 3x + y)}{(n_{CO} + x - y)(n_{H_2O} - x - y)} \quad \text{(b)}$$

The results of the calculations (of the conversion of pure methane) performed in accordance with Eqs. (a) and (b) are shown in Fig. 190 (solid lines) *, from which the following conclusions can be made.

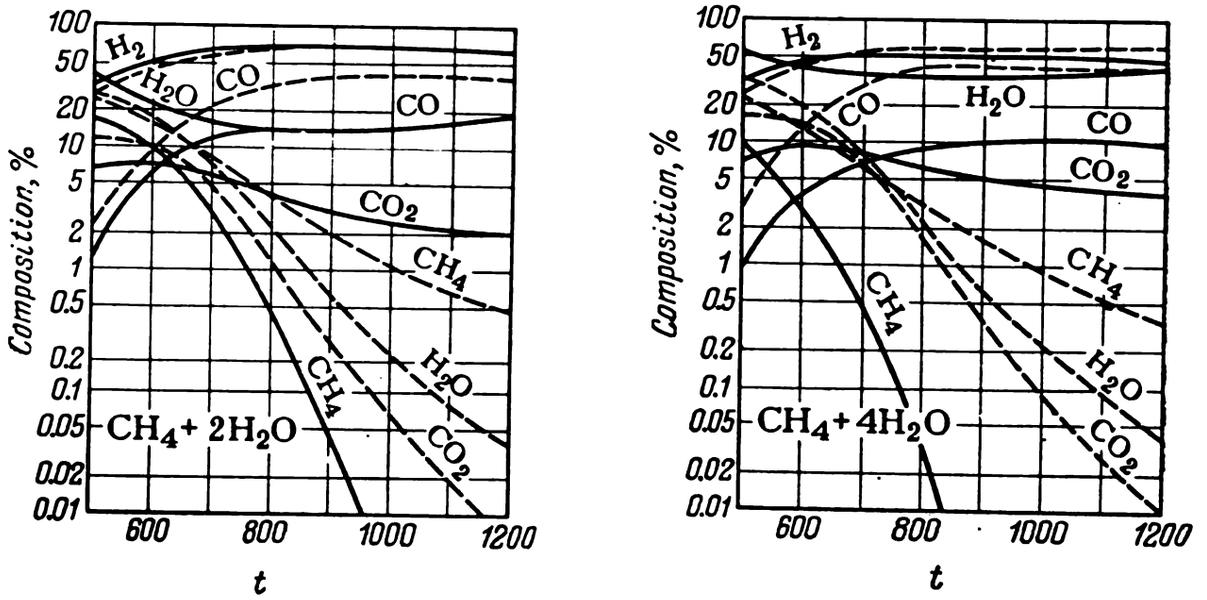

Fig. 190. Influence of temperature on the equilibrium composition of a gas mixture in the conversion of methane with steam.

The dashed lines show conversion in the presence of carbon. (See Example 18)

1. With elevation of the temperature, the conversion of methane proceeds more completely. This is explained by the fact that with a growth in temperature, endothermic reaction (1) is displaced to the right.

2. A surplus of steam favours conversion and simultaneously results in a greater content of carbon dioxide.

3. If the temperature is low and a great surplus of steam is fed into the converter, the reaction mainly follows Eq. (3), and only to an insignificant extent does it follow Eq. (1). Conversely, at high temperatures ($t > 1000$ °C) and with a small surplus amount of steam, the reaction mainly follows Eq. (1).

4. Complete conversion can be achieved only with a very great surplus of steam, because although methane does decompose almost

* The results of investigations by V. Karzhavin and A. Leibush were used in constructing these and the following graphs. Although more accurate thermodynamic data (used, particularly, in solving some of the preceding examples) appeared after the publication of their reports, the results have not changed in principle.

completely at high temperatures, the gas contains a lot of carbon monoxide, which also has to be converted subsequently.

5. To conduct virtually complete conversion, we must have $t > 800\,°C$ at an initial ratio of $[CH_4] : [H_2O] = 1 : 2$ and $t > 700\,°C$ at an initial ratio of $[CH_4] : [H_2O] = 1 : 4$. In industrial conditions, the working temperatures must be considerably higher and be varied depending on the volume rates of flow of the gas and the activity of the catalysts.

It is more rational to conduct the industrial conversion of methane in two stages: first completely convert the CH_4 to CO, and then, at a lower temperature (about 500 °C), the CO to CO_2.

Assume that 90% of the CO formed in the first stage can be converted in the second. Hence the content of methane that has not reacted in the first stage and remains after condensation of the steam, removal of the CO_2 and the residues of the CO will be determined by the expression

$$[CH_4]_{res} = \frac{n'_{CH_4}}{n''_{CH_4} + n'_{H_2} + 0.9n'_{CO}} \times 100\%$$

where the superscripts ′ and ″ indicate the first and second stages, respectively. The results of calculations by this equation are depicted in Fig. 191 (solid lines); they show that high-temperature conversion should be conducted at from 800 to 1000°C in industrial conditions.

Up to now, we have assumed that the process of conversion proceeds homogeneously. Let us see whether it can proceed heterogeneously (with the liberation of carbon), i.e. according to the following reactions:

$$CH_4 = C + 2H_2 \quad (4)$$

$$2CO = CO_2 + C \quad (5)$$

$$CO + H_2 = C + H_2O \quad (6)$$

If one of these reactions is possible, the others must also proceed, because Eqs. (4), (5) and (6) introduce

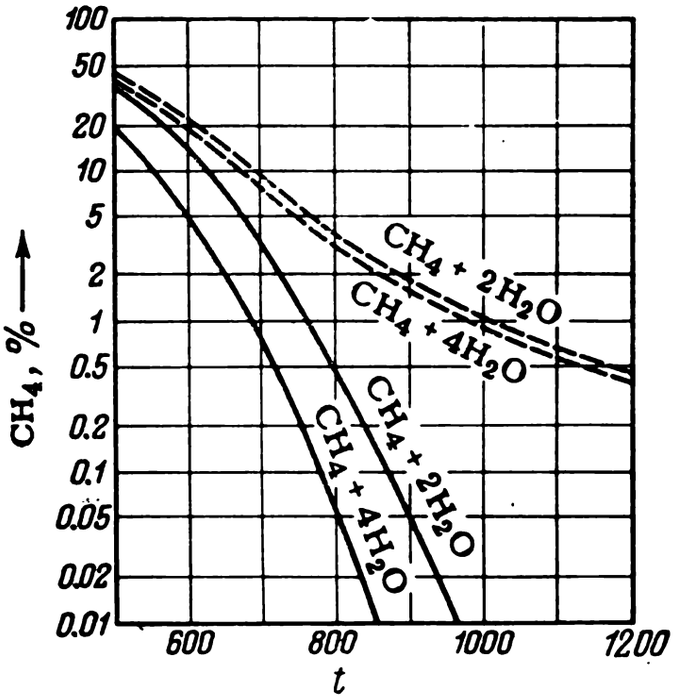

Fig. 191. Influence of temperature and the surplus of steam on the amount of unreacted methane remaining in the equilibrium mixture after the condensation of the steam and the removal of the CO and CO_2.

The dashed lines show conversion in the presence of carbon. (See Example 18)

only one new component — carbon. Therefore all three equations are needed to determine the composition of the equilibrium mixture in the new conditions. We choose Eq. (4) as the new one in addition to Eqs. (1) and (2). For this reaction, Eq. (13.3) becomes

$$\Delta G_4 = 4.576T \log \frac{p_{H_2}^2}{p_{CH_4}} - 4.576T \log (K_p)_4 \qquad (c)$$

The problem of the possibility of cracking methane and, consequently, of the proceeding of reactions (5) and (6) consists in the sign of ΔG_4. This quantity at p = const may differ depending on T, p_{H_2} and p_{CH_4}. Inserting in Eq. (c) the values* of ΔG_4° and the corresponding values of p_{CH_4} and p_{H_2}, we calculate ΔG_4. The calculations can be performed as follows. We determine p_{CH_4} and p_{H_2} for the given degree of decomposition of the CH_4. If we denote the amount of CO_2 formed according to reaction (2) by z, then

$$(K_p)_2 = \frac{(n_{CO_2} - z)(n_{H_2O} - z)}{z(n_{H_2} - z)}$$

whence

$$z = -[(K_p)_2 n_{H_2} + n_{CO} + n_{H_2O}] + \frac{\sqrt{[(K_p)_2 n_{H_2} + n_{CO} + n_{H_2O}]^2 - 4\{[(K_p)_2 - 1] n_{CO} \cdot n_{H_2O}\}^2}}{2[(K_p)_2 - 1]}$$

Introducing into the last equation the values of $(K_p)_2$ and the mole fractions of CO, H_2O and CO_2 (corresponding to the given degree of decomposition of the CH_4), we find the amount of CO_2 formed, and hence that of H_2 [according to reaction (2)]. After this, we determine the values of p_{H_2} and p_{CH_4} (as previously, the total pressure is taken equal to 1 atm).

The results of the calculations are given in Fig. 192. They show that a lower content of steam and a lower temperature are attended by a diminishing of the probability of the liberation of carbon. The liberation of carbon becomes impossible even before equilibrium of reactions (5) and (6) sets in. Indeed, a glance at Fig. 192 shows that, for example, at 600 °C carbon cannot be liberated after 55% of the methane has reacted, while the equilibrium degree of transformation of the CH_4 at this temperature (see Fig. 190) is $(33.3 - 10) \times 100/33.3 = 70\%$; for 800 °C we have 90% and $(33.3 - 0.4) \times 100/33.3 = 99\%$, respectively, etc. Therefore, for all temperatures and with a surplus of steam we have $\Delta G > 0$, which points to the impossibility of reaction (4), and together with it of reactions (5) and (6).

* The accurate values of ΔG_4° can be taken from the initial conditions of Example 4, Chap. 13 (p. 445).

The liberation of carbon is possible only at the beginning of a reaction, i.e. before equilibrium sets in, and also with a very small initial amount of steam. In both cases, the first term of the right-hand side of Eq. (c) is negative and in its absolute value may be greater than the second, as a result of which $\Delta G < 0$.

The practical completeness of a reaction depends on the rate of the processes. Experiments have shown that the decomposition of CH_4 is greatly retarded as H_2 is formed, and it is practically impossible to reach equilibrium in the absence of a catalyst. The false equilibrium that sets in during the experiments differs considerably from the true value.

Although elevation of the temperature increases the probability and rate of the reaction of carbon liberation, it simultaneously accelerates the reaction of CH_4 with H_2O. The result is a lowering of the concentration of the CH_4 and a diminishing of the probability and also of the rate of carbon liberation.

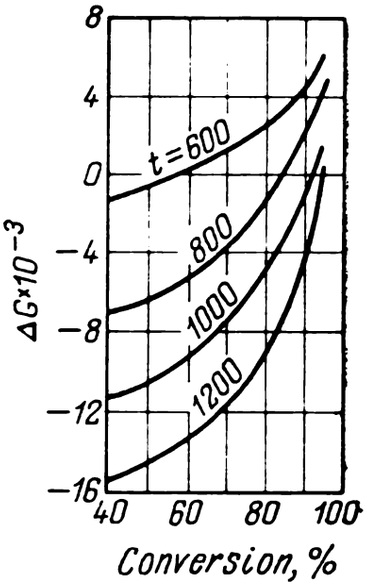

Fig. 192. Change in the probability of liberation of carbon in the conversion of methane with steam.
(See Example 18)

Figure 193 shows approximately the region of carbon liberation (when CH_4 is heated with H_2O in the ratio 1 : 2). This region should expand quite considerably when the amount of steam is decreased.

Finally, in addition to the influence of temperature and concentrations, account must also be taken of the rate of gasification of the carbon formed, which may be liberated at the beginning of the reaction when the concentration of the methane is sufficiently great.

The introduction of coke into the system as a catalyst will cause reaction (4) to shift to the left, and equilibrium will be displaced in the unfavourable direction. To calculate equilibrium in the presence of carbon, we must compile a system of six equations (according to the number of partial pressures). Three of them relate the

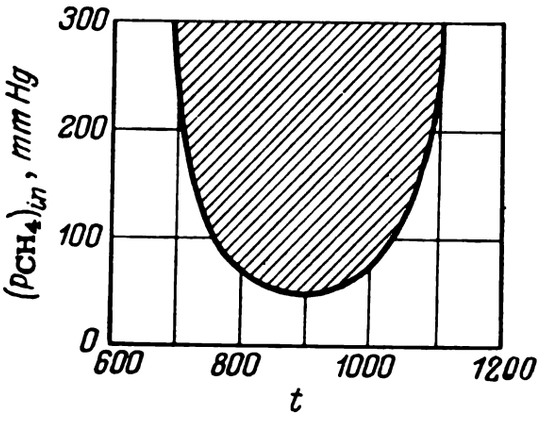

Fig. 193. Influence of temperature and methane content in initial mixture on the liberation of carbon. The zone of liberation of carbon is shaded.
(See Example 18)

constants of Eqs. (1), (2) and (4) to the corresponding partial pressures, the fourth can be written in the form

$$p = p_{CH_4} + p_{H_2O} + p_{CO} + p_{CO_2} + p_{H_2}$$

and the last two should express the correspondence of the equilibrium composition to the composition of the mixture before conversion (a similar procedure was used in solving the preceding example).

The results of calculations given in Figs. 190 and 191 (the dashed curves) show that the presence of carbon considerably lowers the degree of conversion. Thus, at $t = 800\,°C$ and at $[CH_4] : [H_2O] = 1 : 2$, the equilibrium content of CH_4 in the presence of C and without it is 3.5 and 0.4%, respectively; at 900 °C the relevant figures are 2.0 and 0.04%. Inspection of these figures also shows that although raising of the temperature in the given case also increases the degree of conversion, this occurs at a much slower rate than in the absence of carbon. The same effect is obtained when a surplus amount of steam is introduced.

The action of the carbon is due to a shifting of reactions (4), (5) and (6) to the left, the result being a lowering of the content of CO_2 and H_2O and an increase in the content of CH_4 and CO. In the presence of coke, it is also recommended to conduct conversion in two stages. Having performed calculations similar to those on p. 559 and constructed a similar graph (see Fig. 191, the dashed lines), we shall find that even at a high temperature (1000 °C and higher) an equilibrium mixture will contain up to 1% of CH_4. The concentration of CH_4 can be lowered only by considerably raising the temperature, because the introduction of a great surplus of steam has almost no effect. Therefore, if the production of methane is organized to produce pure hydrogen (for example for the synthesis of ammonia), it is impossible to convert it on carbon. If the methane is converted for other purposes [for instance for the preparation of mixtures to be used in organic synthesis (the production of alcohols, synthin, etc.)], the conversion may be conducted on hot coke.

With respect to the consumption of energy, the high-temperature variant of conversion ($t = 900\,°C$) is more advantageous than the low-temperature variant ($t = 700\,°C$). Thus, calculations for natural gas (90% of CH_4, 5% of CO_2 and 5% of H_2) show that the heat needed for low-temperature conversion is 30% greater than that for the high-temperature process.

14.5. SOURCES OF ERRORS IN CALCULATING EQUILIBRIUM

14.5.1. Errors Due to Inaccuracy of Experimental Data

Great errors may be the result of non-isothermal conditions in measuring equilibrium, and also of the displacement of equilibrium because of insufficiently rapid removal of the equilibrium mixture

from the high-temperature reaction zone (in order to inhibit equilibrium).

The error in the values of K_a may also become considerable when the conditions of an experiment do not favour the measurement of equilibrium. Thus, if a reaction is greatly displaced to either side, i.e. if the equilibrium constant is very great or, conversely, very small, the analytical determination of the equilibrium concentrations of the reactants (in the first case) and the products (in the second) becomes very difficult and inaccurate, and the equilibrium constants calculated according to the concentrations become unreliable.

A very low rate of a reaction, when it is practically impossible to reach equilibrium, may be a source of errors. If a catalyst is introduced to accelerate a reaction, new errors may appear due to possible overheating of the catalyst, proceeding of the reaction outside the zone of its action and a difference in the rate of diffusion, which will affect the composition of the mixture formed. A very high rate of a reaction, in turn, results in serious difficulties when analysing the equilibrium of the mixture. In addition, the reaction being studied may not reach the state of equilibrium. The criterion of equilibrium having been reached is usually the unchanging composition of the mixture leaving the reaction zone notwithstanding the change in the rate of volume flow. Cases are known, however, when the composition of a system does not change even when the rate of volume flow diminishes, although equilibrium is absent. In such cases, the reaction should be conducted in both directions if possible.

Errors may appear if no account is taken of the influence of a high pressure (for instance in determining the equilibrium constant by measuring the density of an equilibrium gas mixture), of the influence of the degree of comminution, etc.

Inaccurate values of ΔH are a source of much greater errors, as a rule, than errors in the values of S, even if the entropy has been assessed by calculations.

Great errors are caused by inaccurate values of ΔH_{comb}, especially for reactions of isomerization (see Sec. 3.1). Thus, until comparatively reliable data were obtained for the heat of combustion of methanol, the discrepancies between the calculated and experimentally found values of the equilibrium constant for the reaction

$$CO + 2H_2 = CH_3OH(g)$$

were very great. Calculations show that it is sufficient to assume that ΔH_{comb} of ethene is only 1% higher than the most authentic value of this quantity for $(K_a)_{600}$ for the reaction

$$C_2H_4 + H_2O(g) = C_2H_5OH(g)$$

to change 17 times, and $(K_a)_{300}$ — 300 times.

Inaccuracies in the values of ΔC_p are also a source of errors. For low-temperature processes, inaccuracies in C_p and ΔC_p do not result in great errors in $\Delta G°$, but at elevated temperatures (for example when calculating metallurgical processes, and especially combustion processes), results having a low reliability may be obtained.

The reliability of the results of indirect calculations of K_a or $\Delta G°$ (see Sec. 13.5.1) depends on the accuracy with which these quantities can be determined in the reactions used for the calculations. Therefore, if the required quantity is not great, the error may become quite considerable, especially if separate errors have identical signs.

Upon calculating equilibrium on the basis of data obtained when conducting a reaction in a galvanic cell, attention should be given to the accuracy of measuring the e.m.f., because an insignificant error may lead to an error in $\Delta H°$ exceeding the possible error of most calorimetric data [see Eq. (13.2)].

14.5.2. Errors Connected with the Processing of Experimental Data

Errors may appear as a result of using an equation which is not accurate for the conditions of an experiment, for instance Eq. (14.8) for real solutions or Eq. (14.7) for gas reactions at high pressures. The errors in calculating gas equilibrium at high pressure by Eq. (14.7) may also show, for example, on the graph of $\log K_p$ against T^{-1}, where even for a comparatively small temperature interval the points may be arranged along a curve, notwithstanding the constancy of $\Delta H°$. The opposite case is naturally also not excluded, when the straightness of the line $\log K = \varphi(T^{-1})$ is due to compensation of the changes in K_p with p and in $\Delta H°$ with T.

Therefore, before choosing an approximate equation, the value of the deliberately introduced error must be assessed by comparing it with the reliability of the initial data and with the required accuracy of the results of the calculations.

If Fig. 163 is used to calculate K_a by extrapolation, only the values of K_a in direct proximity to the experimentally found values will be reliable. This is explained by the possible curvature of the lines $\log K = \varphi(T^{-1})$ because of a change in $\Delta H°$ with T, and also by the fact that a break in the straight line may be observed, because within a certain comparatively small temperature interval one reaction may be superseded by another, and $\Delta H°$ will change accordingly. Consequently, extrapolation within a broad temperature interval is not dependable. Experimental data may also give a curvature within a comparatively insignificant temperature interval on the graph of $\log K_a = \varphi(T^{-1})$, which may be due to several causes: either the heat effect of the reaction is not great and there-

fore its relative change will be considerable, or the values plotted on the graph do not correspond to a state of equilibrium. Although an accurate expression $K_a = \varphi(T)$ is obtained when the temperature dependence of $\Delta H°$ is taken into consideration, this complication is superfluous for an insignificant temperature interval: the difference between the equilibrium constants found by the approximate and accurate equations, as a rule, is less than the error of calorimetric determination of $\Delta H°$.

A diminishing of the temperature interval allows us to disregard the temperature dependence of $\Delta H°$, but too small intervals should never be chosen: when the difference $T_2 - T_1$ is very low, the difference between the values of $(K_a)_{T_1}$ and $(K_a)_{T_2}$ may be of the same order of magnitude or greater than the error in determining the equilibrium constant. For this reason, it is good to take a temperature interval of at least 20 kelvins. The maximum permissible interval in each separate case depends on how greatly $\Delta H°$ changes with T.

Calculations of equilibrium even by the accurate equations (13.20) and (13.21) may lead to considerable errors if the integration constant I is calculated according to one value of $(K_a)_T$. An error in the latter quantity results in the inaccuracy of the equation used for calculating temperatures differing considerably from T. This is especially probable when I is very great. It should be noted, however, that at a low value of I good results may not always be obtained, because in this case the product IT loses the "buffer" action it has in a number of cases. Therefore, when several values of K_a for different temperatures are available, it is good to resort to finding the mean value of T or use the procedure of calculations with the aid of the sigma-function treated in Sec. 13.4.2 [Eq. (13.26)].

As regards the constant $\Delta H_0°$, it should be calculated according to equilibrium data if possible. Owing to the absence of the required values, it often becomes necessary to assume that $\Delta H° = \Delta H°_{298} = \Delta H_0°$ ($\Delta C_p = 0$), i.e. use Eqs. (13.11), (13.12) and (13.15). For solutions where $\Delta H°$ is related to the partial molar heat of solution and dilution (which is unknown in the majority of cases), ΔC_p may differ quite considerably from zero. Great errors may also be the result of using different equations $C_p = \varphi(T)$ in the equations $\Delta H° = \varphi(T)$ and $\Delta G° = \varphi(T)$ when the latter two are used jointly.

Although the different accuracy of the various quantities in the equations used for calculations cannot be eliminated, we can consider that the equation $\Delta G° = \varphi(T)$ will be sufficiently reliable in the following cases: (1) if it has been obtained on the basis of authentic experimental values of K_a and ΔH; (2) if the constant $\Delta H_0°$ has great values; (3) if $\Delta G°$ has the same sign as the integration constant I; and (4) if ΔC_p during a reaction is minimum.

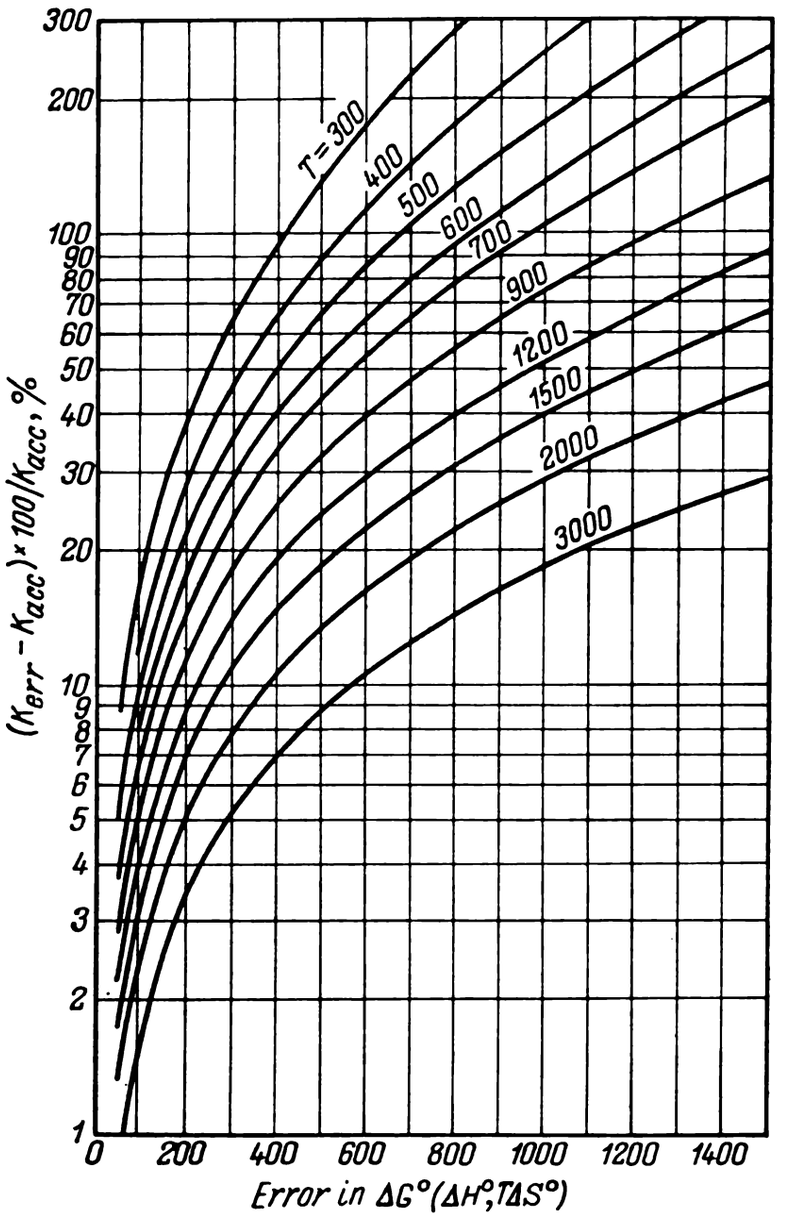

Fig. 194. Relationship between the error in the values of the equilibrium constant and in ΔG° (ΔH°, $T\Delta S^\circ$)

To assess the error in ΔG° due to inaccuracy of the equilibrium constant, we can use Fig. 194. Examination of it shows that even with a low accuracy of K_a the error in ΔG° in many cases is within the error of the heat effects (approximately equal to ± 0.5 to 1 kcal). Thus, an error in K_a even equal to 100% gives an error in ΔG° of only 560 cal for $T = 400$ K.

14.6. THEORETICAL AND PRACTICAL EXTENTS OF A REACTION

Everything said above related to equilibrium systems. This is why we always dealt with the *maximum* possible degree of transformation. In practical conditions, however, reactions seldom reach

equilibrium, and their extent depends on many factors, primarily on the rate of the relevant process. This is especially important when a number of reactions occur simultaneously or consecutively. Therefore, ignoring the kinetics of a process may result in great errors and also in unintentional derogation of the significance of thermodynamics in solving practical problems. We cannot, for example, use the calculated values of the equilibrium constants to explain the values of the yields in complex processes without taking into consideration the fact that a greater or smaller yield of products may be due not only to the values of K_a, but also to the rate of the processes (see Example 18).

Sometimes the substances which should have been obtained as a result of a reaction at a given temperature, pressure and concentration do not form. Instead of the assumed reaction, a different one occurs, even though the conditions are unfavourable for it. This may indicate that the first reaction has a negligible rate in the given conditions, whereas the second reaction proceeds very rapidly. It is clear that the increase in the duration of a process in such cases causes the composition of the mixture to change.

Since the practical extent of a reaction depends on the duration of the process, all the factors increasing the rate of the reaction also increase its extent during any interval of time insufficient for equilibrium to set in. The temperature, pressure and concentration of the reagents are common factors affecting both the kinetics and the statics of processes. For example, if elevation of the temperature is attended by diminishing of the value of K_a, while the rate of the reaction grows, we cannot predict the total action of the change in temperature on the practical extent of the reaction without calculating the rates. The presence of a catalyst makes it possible to use a higher temperature, and, other conditions being equal, the greater the activity of the catalyst, the higher the temperature that can be used (provided, of course, that elevation of the temperature does not lower the activity of the catalyst). It must be noted that a less negative value of ΔG should correspond to the interaction of the catalyst with the reagents than that in the process being catalyzed.

An increase in pressure may also cause opposite results. An increase in pressure is attended by a growth in concentration, and this usually causes the rate of the reaction to grow. If a process occurs with an increase in volume, however, we do not know what the overall result will be. In such cases, a certain optimal pressure should be chosen. Dilution with inert gases also gives different results.

In addition to the above factors, others such as the content of catalyst poisons in the system and the thermal stability of the catalysts must also be taken into consideration.

Chapter 15

FUNDAMENTALS OF QUANTUM STATISTICAL CALCULATIONS OF THERMODYNAMIC FUNCTIONS AND CHEMICAL EQUILIBRIUM FROM SPECTROSCOPIC DATA

15.1. INTRODUCTION

Statistical thermodynamics, which appeared on the basis of t kinetic theory of matter, makes it possible to use directly the properties of molecules obtained by spectroscopic investigations to find the absolute values of the thermodynamic properties for a considerable number of substances and calculate equilibrium without resorting to time-consuming and costly calorimetric measurements at low temperatures. The results are sometimes more accurate than those obtained in other ways, particularly by calculations according to the third law of thermodynamics.

The equations of statistical thermodynamics can be applied to ideal gases, i.e. to conditions when $p \to 0$. To indicate this, all the relevant quantities will be noted by the superscript °. When these equations are applied for high pressures, the corresponding recalculations are needed [for example by Eq. (6.56) for heat capacity, Eq. (6.57) for enthalpy, and Eq. (13.56) for entropy].

The total energy which molecules of a gaseous substance possess can be divided into translational and intramolecular. The latter consists of rotational energy (rotation of a molecule about its centre of gravity), vibrational energy (the energy of vibrations of atoms and groups of atoms in a molecule), electronic (the energy of electron excitation), the energy of spins (the energy of orientation of the magnetic moments) of atomic nuclei in the electromagnetic field of a molecule, and the "zero energy" (the energy at $T = 0$ consisting of the energy of the chemical bond and the zero vibrational energy).

If the energy of a substance is known for different temperatures, we can find the remaining thermodynamic properties. Indeed, by Eqs. (3.10), (4.20), (2.10) and (6.7), we have

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$S = \int \left(\frac{\partial U}{\partial T}\right)_V d \ln T$$

$$H = U + RT$$

But in addition to the energy levels of molecules known from spectroscopic data, to determine the thermodynamic properties of a substance, we must know the distribution of the molecules among these levels. This is given by quantum mechanics.

If two energy levels (terms) are characterized by the energies ε and ε', the number of molecules of an ideal gas n and n' having these energies is determined by the **Maxwell-Boltzmann distribution law**

$$n' = n \exp\left(-\frac{\varepsilon' - \varepsilon}{kT}\right) \tag{15.1}$$

Let the number of molecules having a minimum energy, i.e. at a lower (unexcited) energy level (we shall take it as the "zero" level), equal n_0, hence the number of molecules at the i-th level by Eq. (15.1) will be

$$n_i = n_0 \exp\left(-\frac{\varepsilon_i}{kT}\right)$$

where ε_i is the excess energy in comparison with the zero value.

It follows from Eq. (15.1) that (1) a given state is the more probable, the lower is its energy level; (2) at $T \to 0$ all the molecules pass over to a lower energy level; (3) the probability of high energy levels grows with increasing temperature; and (4) at very high temperatures, when $T \gg (\varepsilon' - \varepsilon)/k$, the distribution is almost uniform.

Depending on the frequency of absorbed radiation, a molecule can be excited in different ways. The nature of the phenomena occurring, which can be assessed by analysis of the spectrum, is due to the values of the supplied energies.

The energy needed for exciting different degrees of freedom is different: if an energy of the order of magnitude of 10^{-21} cal/mol is needed to excite translational degrees of freedom, then from 10^1 to 10^2 cal/mol are needed for rotational, from 10^3 to 10^5 for vibrational, and 10^8 cal/mol for electronic degrees of freedom. Therefore, at ordinary temperatures, the translational and rotational degrees of freedom are excited completely, the vibrational degrees of freedom are excited only at elevated temperatures, while excitation of the electronic levels requires very high temperatures.

Some states have energies so close that it is practically impossible to distinguish them (this holds for all temperatures except very

low ones). It is therefore good to combine them and assign to them a **statistical weight** g_i equalling the number of all the separate states included, and consider that the quantity g_i equals the number of sublevels into which a given level of intramolecular energy ε_i decomposes, i.e. it can be considered as the multiplicity ("degeneracy") of a given energy level manifesting itself as a result of disturbing factors (for instance the action of adjacent molecules). Thus, the statistical weight is the number of possible quantum states having the same or almost the same energy. It can be considered as the probability P of a state with the energy ε_i.

Disregarding the insignificant difference between the sublevel energies, i.e. considering that the terms $\exp(-\varepsilon_i/kT)$ practically coincide for them, we shall find that the number of molecules in a given energy state equals $g_i \exp(-\varepsilon_i/kT)$. Since the number of molecules at all the levels must equal their total number, for one mole we get

$$N_A = \sum n_i g_i = g_0 n_0 + g_1 n_0 \exp\left(-\frac{\varepsilon_1}{kT}\right) + \\ + g_2 n_0 \exp\left(-\frac{\varepsilon_2}{kT}\right) + \ldots \qquad (15.2)$$

where N_A is the Avogadro constant.

The quantity

$$Q \equiv \sum g_i \exp\left(-\frac{\varepsilon_i}{kT}\right) \qquad (15.3)$$

characterizing the distribution of molecules among the energy levels is called the **partition function.** It is the basis for the method of calculations being considered. It will be shown below that the calculation of thermodynamic properties consists in finding Q and its derivatives with respect to temperature.

To calculate Q, we must know the energy levels and the statistical weights, which are determined by the results of spectroscopic investigations and by the structure of the molecules. It is therefore necessary to first conduct spectroscopic observations, next assume a quantum mechanical model of a molecule, then decipher the spectroscopic data in accordance with the adopted model and, finally, find the distribution of the energy by levels.

Accurate calculations require thorough studying of the spectrum of a substance (both the Raman and the infrared spectra), a detailed and unambiguous interpretation of all the spectrum lines and their distribution among the different series; finding of formulas for calculating the vibration frequencies and, finally, the most difficult task performed by methods of statistical mechanics, finding of

the statistical weights of the levels. Account must also be taken of the mutual influence of the various energy levels.

Accurate calculations present no difficulties for monoatomic and most of the diatomic molecules. Only approximate calculations are almost always the only possibility for polyatomic (even triatomic) molecules, notwithstanding the availability of special tables that considerably facilitate some calculations. The approximate method of calculations often gives results that are virtually identical with the accurate ones.

We shall limit ourselves only to a brief treatment of the approximate method, considering that the data on the structure of molecules are known. We shall also assume that the spectrum of a substance is available, and that a quantum mechanical model of a molecule has been adopted, in accordance with which the spectrum has been deciphered and the energy levels have been indicated.

For the majority of molecules beginning from $T \approx 50$ and up to about 5000 K, we can assume that

$$Q = Q_{\text{trans}} Q_{\text{intra}} = Q_{\text{trans}} Q_{\text{rot-vib}} Q_{\text{e}} Q_{\text{nuc}} \tag{15.4}$$

i.e. the mutual influence of the rotational-vibrational, electronic and nuclear (nuclear spin effect) partition functions is not great. Moreover, owing to the difficulty of taking into account the mutual influence of rotations and vibrations (especially the influence of vibrations on the moments of inertia of the molecules), we shall consider this influence to be negligible, which generally results in a small error. Consequently, we shall assume that

$$Q = Q_{\text{trans}} Q_{\text{rot}} Q_{\text{vib}} Q_{\text{e}} Q_{\text{nuc}} \tag{15.5}$$

The form of Eqs. (15.4) and (15.5) is determined by the exponential nature of the function Q [see Eq. (15.3)] : addition of the energies corresponds to multiplication of the partition functions. Thus, in accordance with Eq. (15.5), we assume the additivity of the energy :

$$\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{e}} + \varepsilon_{\text{nuc}} + \varepsilon_0$$

Finally, summation of the function Q by terms according to different degrees of freedom is replaced by integration for simplicity. The other simplifications will be indicated in each separate case.

Owing to the adopted mutual independence of Q_i, the calculations for each degree of freedom are performed separately. It is also obvious that by summation of the values of the relevant thermodynamic properties found according to the values of Q_i, we shall get a given property of a gas as a whole.

15.2. THERMODYNAMIC PROPERTIES OF GASES DUE TO TRANSLATIONAL DEGREES OF FREEDOM

The division of energy into that due to translational motion and that due to intramolecular motion is convenient, first, because the change in the entropy, Gibbs and Helmholtz energies of an ideal gas with a change in pressure is due only to translational motion; second, for any polyatomic gas, the thermodynamic properties corresponding to the translational degrees of freedom equal the thermodynamic properties of a monoatomic gas. In particular, for any gas, the energy of translational motion U°_{trans} equals the total value of U° of a monoatomic gas for which in accordance with three degrees of freedom

$$U^\circ_{\text{trans}} = \frac{3}{2} RT = 2.981T \tag{15.6}$$

Hence we get:

by Eq. (3.10)

$$(C^\circ_V)_{\text{trans}} = \frac{\partial U^\circ_{\text{trans}}}{\partial T} = \frac{3}{2} R = 2.981 \tag{15.7}$$

by Eq. (2.10)

$$H^\circ_{\text{trans}} = U^\circ_{\text{trans}} + pV = \frac{3}{2} RT + RT = 4.968T \tag{15.8}$$

by Eq. (3.11)

$$(C^\circ_p)_{\text{trans}} = \frac{\partial H^\circ_{\text{trans}}}{\partial T} = \frac{5}{2} R = 4.968 \tag{15.9}$$

The entropy of a monoatomic gas, if its molecules are at a lower electron level and there is no nuclear spin, is expressed by the following equation, derived by the statistical method:

$$S_{\text{trans}} = R \left[\ln \frac{(2\pi kMT)^{\frac{3}{2}} e^{\frac{5}{2}} V}{h^3 N_A} \right] \tag{15.10}$$

where h = Planck constant
N_A = Avogadro constant.

It follows from this equation that

$$S_{\text{trans}} = \frac{3}{2} R \ln M + \frac{5}{2} R \ln T - R \ln p +$$

$$+ \frac{5}{2} R - 7.282 = 6.8635 \log M + 11.4391 \log T -$$

$$- 4.5756 \log p - 2.313 \tag{15.11}$$

whence

$$S^\circ_{\text{trans}} = 6.8635 \log M + 11.4391 \log T - 2.313 \qquad (15.12)$$

The accuracy of Eqs. (15.10)-(15.12) is confirmed by a comparison of the experimentally found and calculated values of the chemical constants for inert gases and the vapours of certain metals (see Table 15), i.e. of substances whose properties satisfy the conditions observed in deriving Eq. (15.11).

The relationship between entropy and the true chemical constants can be shown as follows.

When a vapour is a monoatomic ideal gas, Eq. (13.41) in accordance with Eq. (15.9) becomes

$$\ln p = -\frac{\Delta H_0^\circ}{RT} + \frac{5}{2} \ln T +$$

$$+ \frac{1}{R} \int \frac{dT}{T^2} \int_0^T C_p^{\text{cd}}\, dT + 2.303j$$

or

$$\ln p = -\frac{\Delta H_0^\circ}{RT} + \frac{5}{2} \ln T + \frac{1}{RT} \int_0^T C_p^{\text{cd}} -$$

$$- \frac{1}{R} \int_0^T \frac{C_p^{\text{cd}}\, dT}{T} + 2.303j \qquad (15.13)^*$$

where the superscript "cd" stands for a condensed phase.

After determining ΔH_0° from the equation

$$\Delta H^\circ = \Delta H_0^\circ + \frac{5}{2} RT - \int_0^T C_p^{\text{cd}}\, dT$$

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* Modification of the term $\frac{1}{R} \int \frac{dT}{T^2} \int C_p^{\text{cd}}\, dT$ was the result of integration by parts; since $\int u\, dv = uv - \int v\, du$, then after introducing $u = \int C_p^{\text{cd}}\, dT$ and $dv = \frac{dT}{T^2}$, we get

$$\int \frac{dT}{T^2} \int C_p^{\text{cd}}\, dT = -\frac{1}{T} \int C_p^{\text{cd}}\, dT - \int \left(-\frac{1}{T}\right) C_p^{\text{cd}}\, dT$$

which is obtained in accordance with Eq. (15.9), we find

$$\ln p = -\frac{\Delta H^\circ}{RT} + \frac{5}{2} + \frac{5}{2}\ln T - \frac{1}{R}\int_0^T \frac{C_p^{cd}\,dT}{T} + 2.303j$$

or

$$\frac{\Delta H^\circ}{T} + \int_0^T \frac{C_p^{cd}\,dT}{T} = \frac{5}{2} R \ln T - R \ln p + \frac{5}{2} R + 4.5756j \qquad (15.14)$$

In all the equations, ΔH° is the heat of vaporization of one mole of the condensed phase. In accordance with Eqs. (4.8) and (13.53), the left-hand side of Eq. (15.14) is the entropy of the vapour in equilibrium with the solid at the temperature T. Considering as previously that the vapour is an ideal gas, we shall have [see, for example, Eq. (b) in the solution of Example 5 in Chap. 6, p. 148] :

$$S_T^g = \int \frac{C_T^g\,dT}{T} - R \ln p + S_0 = \frac{5}{2} R \ln T - R \ln p + S_0 \qquad (15.15)$$

where S_0 is the entropy extrapolated to absolute zero.

Equating the right-hand sides of Eqs. (15.14) and (15.15), we get

$$S_0 = \frac{5}{2} R + 4.5756j$$

or

$$j = \frac{S_0 - \frac{5}{2} R}{4.5756} \qquad (15.16)$$

Equation (15.16) retains its form for polyatomic molecules; the only difference will be that the quantities S_0 and C_p change.

The Gibbs energy is usually calculated by relating it to the value of the energy (entropy) at absolute zero. The introduction of $G^\circ - U_0^\circ = G^\circ - H_0^\circ$ instead of G° (or the corresponding difference instead of A°) is due to the fact that the indefinite constants U_0° and H_0° remain in Eqs. (5.5) and (5.19) (they equal each other, and also the quantities G_0° and A_0° because all of them are independent of the pressure and volume).

In accordance with Eqs. (15.6), (15.8), (15.11) and (5.19), we have

$$(G^\circ - U_0^\circ)_{trans} = (G^\circ - H_0^\circ)_{trans} = -\frac{3}{2} RT \ln M - \frac{5}{2} RT \ln T + RT \ln p + 5.293T \qquad (15.17)$$

or

$$\left(\frac{G^\circ - U_0^\circ}{T}\right)_{\text{trans}} = \left(\frac{G^\circ - H_0^\circ}{T}\right)_{\text{trans}} = -6.8635 \log M - 11.4391 \log T + 5.293 \quad (15.18)$$

The convenience of the latter form of writing down the equation will become obvious from the following.

Example 1. Find the quantities U°_{trans}, $(C^\circ_V)_{\text{trans}}$, H°_{trans}, $(C^\circ_p)_{\text{trans}}$, S°_{trans} and $[(G^\circ - H^\circ_0)/T]_{\text{trans}}$ for C_2H_4 at $t = 25\,^\circ\text{C}$.

Solution. By Eqs. (15.6)-(15.9), (15.12) and (15.18), we get, respectively, $U^\circ_{\text{trans}} = 2.981 \times 298.2 = 889$ cal/mol, $(C^\circ_V)_{\text{trans}} = 2.981$ cal/mol·K, $H^\circ_{\text{trans}} = 4.968 \times 298.2 = 1482$ cal/mol, $(C^\circ_p)_{\text{trans}} = 4.968$ cal/mol·K, $S^\circ_{\text{trans}} = 6.8635 \log 28.052 + 11.4391 \log 298.2 - 2.313 = 36.021$ cal/mol·K, and $[(G^\circ - H^\circ_0)/T]_{\text{trans}} = -6.8635 \times \log 28.052 - 11.4391 \log 298.2 + 5.293 = -32.361$ cal/mol·K.

Example 2. Calculate the value of the true chemical constant for mercury and compare it with the results of Example 14 in Chap. 13 (p. 470).

Solution. From Eq. (15.11) it follows that

$$S_0 = \frac{3}{2} R \ln M + \frac{5}{2} R - 7.282$$

or by Eq. (15.16) we have $j = \frac{3}{2} \log M - 1.592$. Hence $j_{\text{Hg}} = \frac{3}{2} \log 200.61 - 1.592 = 1.862$, which differs from the experimentally found value by 1.7%.

15.3. THERMODYNAMIC PROPERTIES OF GASES DUE TO INTRAMOLECULAR DEGREES OF FREEDOM

The intramolecular energy related to its value at absolute zero U°_0 equals the sum of the products of the internal energy of the separate kinds of molecules and their number, i.e.

$$U^\circ_{\text{in}} - U^\circ_0 = 0 g_0 n_0 + \varepsilon_1 g_1 n_0 \exp\left(-\frac{\varepsilon_1}{kT}\right) + \varepsilon_2 g_2 n_0 \exp\left(-\frac{\varepsilon_2}{kT}\right) + \ldots = n_0 \sum \varepsilon_i g_i \exp\left(-\frac{\varepsilon_i}{kT}\right) \quad (15.19)$$

(because for any state it is obtained by multiplying the energy of each molecule by the number of molecules in the given energy state).

Combining Eqs. (15.2), (15.3) and (15.19) and taking into account that by Eq. (15.3)

$$\frac{dQ}{dT} = \frac{\Sigma \varepsilon_i g_i \exp(-\varepsilon_i/kT)}{kT^2}$$

we get

$$(U^\circ - U_0^\circ)_{in} = (H^\circ - H_0^\circ)_{in} = \frac{N_A \Sigma \varepsilon_i g_i \exp(-\varepsilon_i/kT)}{\Sigma g_i \exp(-\varepsilon_i/kT)} =$$

$$= \frac{RT^2}{Q_{in}} \frac{dQ_{in}}{dT} = RT \frac{d \ln Q_{in}}{d \ln T} \qquad (15.20)$$

Here $(U^\circ)_{in} = (H^\circ)_{in}$ and $C_{in} = (C_{in}^\circ)_p = (C_{in}^\circ)_V$ owing to the independence of these quantities of p and V.

It is easy to find equations for calculating the fraction of the heat capacity, entropy and Gibbs energy due to intramolecular degrees of freedom from Eq. (15.20) and the general thermodynamic relationships given earlier.

From Eq. (3.10)

$$C_V = \frac{1}{T} \frac{dU}{d \ln T}$$

or

$$C_{in}^\circ = \frac{N_A}{kT^2} \left\{ \frac{\Sigma \varepsilon_i^2 g_i \exp(-\varepsilon_i/kT)}{\Sigma g_i \exp(-\varepsilon_i/kT)} - \left[\frac{\Sigma \varepsilon_i g_i \exp(-\varepsilon_i/kT)}{\Sigma g_i \exp(-\varepsilon_i/kT)} \right]^2 \right\} =$$

$$= R \frac{d \ln Q_{in}}{d \ln T} + R \frac{d^2 \ln Q_{in}}{d(\ln T)^2} \qquad (15.21)$$

Since $dS_{in}^\circ = C_{in}^\circ d \ln T$, it follows from Eq. (15.21) that $dS_{in}^\circ = R d \ln Q_{in} + R(d \ln Q_{in}/d \ln T)$.

Because when $(Q_{in})_0 = g_0$, we also have $d \ln (Q_{in})_0/dT = 0$, integration of the found equation yields

$$S_{in}^\circ = R \ln Q_{in} + R \frac{d \ln Q_{in}}{d \ln T} + [(S_0^\circ)_{in} - R \ln g_0]$$

We know that $S_{T=0}^\circ = S_0^\circ$ and $P = g_0$, hence from Eq. (4.26) it follows that

$$S_{in}^\circ = R \ln Q_{in} + R \frac{d \ln Q_{in}}{d \ln T} \qquad (15.22)$$

Finally, by Eq. (15.20) we get

$$\left(\frac{G^\circ - H_0^\circ}{T}\right)_{in} = \left(\frac{A^\circ - H_0^\circ}{T}\right)_{in} = -R \ln Q_{in} \qquad (15.23)$$

The corresponding combination of Eqs. (15.6)-(15.9), (15.12) and (15.18) with Eqs. (15.20)-(15.23) gives the cumulative value of the thermodynamic quantities.

Inspection of the above equations shows that it is easier to calculate the Gibbs energy than the other functions: it is simpler to calculate Q than the derivative dQ/dT in the expressions for energy, enthalpy and entropy, let alone the second derivative in the equation for heat capacities. In accurate calculations, when Q and its derivatives with respect to T are summated, it is not difficult to calculate Q, but finding $d \ln Q/d \ln T$ and especially $d^2 \ln Q/d (\ln T)^2$ is quite time-consuming, because the members of the sum do not become infinitesimal so rapidly.

The application of Eqs. (15.20)-(15.23) to various intramolecular degrees of freedom allows us to calculate the addend of a parameter due to the given degree of freedom. For this purpose, we must know Q_{rot}, Q_{vib}, etc. We shall therefore turn to finding the separate components of Q_{in}.*

15.3.1. Rotational Partition Function

Assume that a molecule is a rigid rotator, i.e. that its dimensions do not change. Quantum mechanics gives us the following equation for a diatomic molecule having two equal moments of inertia:

$$\varepsilon_{rot} = \frac{h^2}{8\pi^2 I} r(r + 1) \qquad (15.24)$$

where r = rotational quantum number

I = moment of inertia with respect to two mutually perpendicular axes passing through the centre of gravity of a molecule perpendicular to its axis.

The quantities r acquire values of 0, 1, 2, ... and are determined by the angular moment of inertia in various rotational states.

The moment of inertia for diatomic molecules equals ml^2, where $m = m_1 m_2/(m_1 + m_2)$ and l is the equilibrium distance between atoms. The moment of inertia is determined either radiographically

* Formulas for calculating the properties due to translational motion (Sec. 15.2) can be found in the same way as was followed to get Eqs. (15.20)-(15.23) if we use the equation $Q_{trans} = (2\pi MkT)^{\frac{3}{2}} eV/h^3 N_A^{\frac{5}{2}}$.

or on the basis of spectroscopic data according to the arrangement of the rotational lines in the infrared spectrum of molecules.

The statistical weight of a given rotational level

$$g_{\text{rot}} = 2r + 1 \tag{15.25}$$

Therefore in accordance with Eq. (15.3), we have

$$Q_{\text{rot}} = \sum_{r=0}^{r=\infty} (2r + 1) \exp\left[-\frac{h^2 r(r+1)}{8\pi^2 I k T}\right] =$$

$$= \sum_{r=0}^{r=\infty} (2r + 1) \exp\left[-ar(r+1)\right] \tag{15.26}$$

where

$$a = \frac{h^2}{8\pi^2 I k T} \tag{15.27}$$

has been introduced to simplify writing of the equation.

For high temperatures, the quantity a is small, and integration may be used instead of summation. Hence Eq. (15.26) will become

$$Q_{\text{rot}} \approx \int_0^{\infty} (2r + 1) \exp\left[-ar(r+1)\right] dr \approx \frac{1}{a} = \frac{8\pi^2 k T}{h^2} I \tag{15.28}$$

This expression holds only for asymmetric diatomic molecules (for example for CO and HCl). For symmetric di-, tri- and polyatomic molecules, we must take into account the presence of symmetry in the structure, owing to which part of the energy levels drops out. Consequently, the symmetry number σ must be introduced into the equation used for calculations as a divisor. It indicates the number of undistinguishable positions when a molecule rotates through 360 degrees and is determined by studying the three-dimensional model of the molecule. For O_2, CO_2 and C_2H_2, for example, $\sigma = 2$; for a pyramidal molecule (for example $AsCl_3$) $\sigma = 3$, because if we rotate a molecule about the axis passing through the As nucleus and the centre of the triangle formed by the Cl nuclei, its position in space will repeat through every 120 degrees; for CH_4 the value of σ is 12, because rotation about each of the axes of a tetrahedron gives three coinciding positions, i.e. $\sigma = 4 \times 3 = 12$.

The symmetry numbers and moments of inertia for selected gases are given in Table 25.

For tri- and polyatomic molecules, the difference between the values of the moments of inertia about the three coordinate axes must also be taken into account, and accordingly an additional change must be introduced into Eq. (15.28). Hence, using integration instead of summation as previously (here this gives an even smaller error, because owing to the increase in the dimensions of

the molecules, the moments of inertia grow and the symmetry number σ diminishes accordingly), we get approximate equations similar to Eq. (15.28), which are given in Table 26.

Table 25. **Symmetry Numbers and Moments of Inertia for Selected Gases**

Gas	σ	$I \times 10^{40}$	Gas	σ	$I \times 10^{40}$ *
Br_2	2	342.5	CO_2	2	70.2
Cl_2	2	113.9	COS	1	13.7
F_2	2	27.8	CS_2	2	24.7
H_2	2	0.463	HCN	1	18.7
I_2	2	741.5	H_2O	2	1.784
N_2	2	13.84	H_2S	2	3.63
O_2	2	19.23	N_2O	1	66.1
CO	1	14.43	SO_2	2	42.5
CN	1	14.62	C_2H_2	2	23.51
HBr	1	3.26	NH_3	3	3.22
HCl	1	2.65	PH_3	3	7.97
HF	1	1.35	CCl_4	12	—
HI	1	4.31	CH_4	12	5.30
NO	1	16.51	C_2H_4	4	17.33
OH	1	1.50	C_2H_6	18	14.7

* Reduced moments of inertia.

By combining the equation for Q_{rot} with Eqs. (15.20)-(15.23), we can find the fraction of the relevant thermodynamic parameter due to rotation of a molecule. Thus, we get:

for diatomic and linear polyatomic molecules

$$(U^\circ - H_0^\circ)_{rot} = (H^\circ - H_0^\circ)_{rot} = RT \tag{15.35}$$

$$(C_V^\circ)_{rot} = (C_p^\circ)_{rot} = R \tag{15.36}$$

$$S_{rot}^\circ = R \ln T + R \ln I - R \ln \sigma + 177.67 \tag{15.37}$$

$$\left(\frac{G^\circ - H_0^\circ}{T}\right)_{rot} = -R \ln T - R \ln I + R \ln \sigma + 174.308 \tag{15.38}*$$

* Equations (15.35)-(15.38) are obtained by combining Eqs. (15.28)-(15.30) with (15.20)-(15.23), because it is obvious that

$$\ln Q_{rot} = \ln T + \ln I - \ln \sigma + \text{const}$$

$$\frac{d \ln Q_{rot}}{d \ln T} = 1 \quad \text{and} \quad \frac{d^2 \ln Q_{rot}}{d (\ln T)^2} = 0$$

Table 26. **Values of Q_{rot} for Different Kinds of Molecules**

Kind of molecule	Examples	Q_{rot}	
Symmetric diatomic	Cl_2, O_2	$\frac{1}{2}\frac{8\pi^2 kT}{h^2} I$	(15.29)
Linear polyatomic (axial symmetry)			
$I_A = I_B = I_C$	CO_2, C_2H_2, HCN	$\frac{1}{\sigma}\frac{8\pi^2 kT}{h^2} I$	(15.30)*
Non-linear polyatomic			
(a) asymmetric			
$I_A \neq I_B \neq I_C$	CH_3OH, H_2O	$\frac{\sqrt{\pi}}{\sigma}\left(\frac{8\pi^2 kT}{h^2}\right)^{\frac{3}{2}} (I_A I_B I_C)^{\frac{3}{2}}$	(15.31)
(b) pyramidal (bipyramidal)			
$I_A = I_B > I_C$	$CHCl_3$, NH_3	$\frac{\sqrt{\pi}}{\sigma}\left(\frac{8\pi^2 kT}{h^2}\right)^{\frac{3}{2}} I_A I_C^{\frac{1}{2}}$	(15.32)
(c) tetrahedral			
$I_A = I_B = I_C$	CCl_4, CH_4	$\frac{\sqrt{\pi}}{\sigma}\left(\frac{8\pi^2 kT}{h^2}\right)^{\frac{3}{2}} I^{\frac{3}{2}}$	(15.33)
Symmetric bipyramids with free rotation about axis C—C			
$I_A = I_B$, $I_C = I_D$	C_2H_6	$\frac{\sqrt{\pi}}{\sigma}\left(\frac{8\pi^2 kT}{h^2}\right) I_A I_C$	(15.34)

* Although this equation coincides with Eq. (15.28) written down for symmetric molecules, here $I = \Sigma m_i l_i^2$, where l_i is the vector distance to the i-th atom from the centre of mass and is determined from the condition $\Sigma m_i l_i = 0$.

for polyatomic non-linear molecules

$$(U^\circ - H_0^\circ)_{rot} = (H^\circ - H_0^\circ)_{rot} = \frac{3}{2} RT \qquad (15.39)$$

$$(C_V^\circ)_{rot} = (C_p^\circ)_{rot} = \frac{3}{2} R \qquad (15.40)$$

$$S_{rot}^\circ = \frac{3}{2} R \ln T + \frac{1}{2} R \ln (I_A I_B I_C) - R \ln \sigma + 267.54 \qquad (15.41)$$

$$\left(\frac{G^\circ - H_0^\circ}{T} \right)_{rot} = -\frac{3}{2} R \ln T - \frac{1}{2} R \ln (I_A I_B I_C) + R \ln \sigma - 264.63 \qquad (15.42)\ *$$

A glance at Eqs. (15-35)-(15-42) shows that difficulties are only encountered in calculating S_{rot}° and $[(G^\circ - H_0^\circ)/T]_{rot}$, because the quantities $(U^\circ - H_0^\circ)_{rot}$ and $(C_p^\circ)_{rot}$ do not include the moments of inertia. While it is a simple matter to find the moments of inertia for symmetric molecules, for complex asymmetric molecules this can be done only by using special methods (see, for example, [C10]). The values of the reduced moments of inertia $I = \sqrt[3]{I_A I_B I_C}$ for selected gases are given in Table 25.

Internal Rotation. In complex molecules, the rotation of one group of atoms relative to another (for example of the group CH_3 about the bond C—C in ethane) must be taken into consideration. Internal rotation may be hindered as well as free, because a molecule has a force field tending to orient a group of atoms in a definite position relative to the other groups. The energy needed to rotate a given group from the position where the force inhibiting rotation is minimum to the position where it is maximum (the difference is due to the change in the distance with a change in the angle of rotation) is called the **energy** or **potential barrier (hindering potential).**

When there is internal rotation, the rotational partition function equals the product of Q_{rot} and $Q_{i.rot}$. The partition function of internal rotation

$$Q_{i.rot} = \left(\frac{8\pi^3 kTI}{h\sigma_{i.rot}} \right)^{\frac{1}{2}} \qquad (15.43)$$

* Equations (15.39)-(15.42) are obtained by combining Eqs. (15.31) with Eqs. (15.20)-(15.23), because it is obvious that

$$\ln Q_{rot} = \frac{3}{2} \ln T + \frac{1}{2} \ln (I_A I_B I_C) - \ln \sigma + \text{const}$$

$$\frac{d \ln Q_{rot}}{d \ln T} = \frac{3}{2} \quad \text{and} \quad \frac{d^2 \ln Q_{rot}}{d(\ln T)^2} = 0$$

where I = reduced moment of inertia of internal rotation
$\sigma_{i.rot}$ = symmetry number of internal rotation equal to the number of positions of maximum attraction between the atoms and rotating groups in rotation through 360 degrees. (For C_2H_6, for example $\sigma_{i.rot} = 3$, i.e. during one revolution the hydrogen atoms of one CH_3 group occupy a position corresponding to the minimum distance from a hydrogen atom of the other CH_3 group three times.)

For two groups rotating relative to one of the axes of the molecules, I is found by the equation

$$I = \frac{I_A I_B}{I_A + I_B} \tag{15.44}$$

where I_A and I_B are the moments of inertia of the groups rotating about this axis.

The values of $(U^\circ - H_0^\circ)_{i.rot}$, $(C_p^\circ)_{i.rot}$, $S_{i.rot}^\circ$ and $[(G^\circ - H_0^\circ)/T]_{i.rot}$ are determined by Eqs. (15.43) and (15.20)-(15.23).

The thermodynamic functions for hindered rotation are determined with the aid of specially compiled tables (see, for example, [B56], [C10], [D47]. They give values of $S_{fr.i.rot}^\circ - S_{h.i.rot}^\circ$, $C_{h.i.rot}^\circ$, etc. as functions of V/RT and $1/Q_{i.rot}$ (or n^2/IV), where V is the hindering potential and n is the number of maxima of the hindering potential during one complete revolution ($n = \sigma_{i.rot}$).

The value of the potential barrier preventing internal rotation is as a rule several thousand calories (for instance for $CH_3—CH_3$ it is 3150 and for $CH_3—OH$ it is 2700 cal/mol). For double and triple bonds, internal rotation is almost completely suppressed, and it can be considered as vibration (see below).

The contribution to the corresponding thermodynamic property due to internal rotation is added to the thermodynamic property due to the other degrees of freedom. If a molecule contains several groups performing internal rotation, the calculations are performed for each of them, and then the results are summated.

Example 3. Find the quantities $(U^\circ - H_0^\circ)_{rot}$, $(C_p^\circ)_{rot}$, S_{rot}° and $[(G^\circ - H_0^\circ)/T]_{rot}$ for C_2H_4 at $t = 25\,^\circ C$.

Solution. Using Eqs. (15.39)-(15.42) for our calculations, we get $(U^\circ - H_0^\circ)_{rot} = 889$ cal/mol, and $(C_p^\circ)_{rot} = 2.981$ cal/mol·K. Using the data of Table 25, we get

$$S_{rot}^\circ = \frac{3}{2} R \ln 298.2 + \frac{1}{2} R \ln (17.33 \times 10^{-40})^3 - R \ln 4 + 267.54 =$$

$$= 15.80 \text{ cal/mol} \cdot \text{K}$$

and

$$\left(\frac{G^\circ - H_0^\circ}{T}\right)_{rot} = -\frac{3}{2} R \ln 298.2 - \frac{1}{2} R \ln (17.33 \times 10^{-40})^3 + \\ + R \ln 4 - 264.63 = -12.89 \text{ cal/mol} \cdot \text{K}$$

Example 4. Use tables given in [D47] to find the values of the thermodynamic functions due to hindered internal rotation for CH_3OH at $t = 25\,^\circ C$ if $I_{CH} = 5.203 \times 10^{-40}$, $I_{OH} = 1.344 \times 10^{-40}$, $\sigma_{i.rot} = 3$ and $V = 2700$ cal/mol.

Solution. By Eq. (15.44) we have

$$I = \frac{(5.203 \times 10^{-40})(1.344 \times 10^{-40})}{5.203 \times 10^{-40} + 1.344 \times 10^{-40}} = 1.068 \times 10^{-40}$$

For $T = 298.2$, $I = 1.068 \times 10^{-40}$, $\sigma = 3$ and $V = 2700$, we get

$$\frac{V}{RT} = 4.557 \quad \text{and} \quad \frac{10^{-36}(\sigma_{i.rot})^2}{IV} = \\ = \frac{10^{-36} \times 3^2}{1.068 \times 10^{-40} \times 2700} = 31.2$$

Interpolation in Table 14 of ([D47], Vyp. 1:130) gives $S^\circ_{fr.i.rot} - S^\circ_{h.i.rot} \approx 0.92$, since $S^\circ_{h.i.rot} = S^\circ_{i.rot} - (S^\circ_{i.rot} - S^\circ_{h.i.rot})$, then in accordance with Eqs. (15.22) and (15.43) we have

$$S^\circ_{h.i.rot} = \frac{1}{2} R + R \ln Q_{rot} - (S^\circ_{i.rot} - S^\circ_{h.i.rot}) = 1.01$$

Next using Tables 15-17 of ([D47], Vyp. 1:130-131) we calculate $G^\circ_{i.rot} - G^\circ_{h.i.rot} = 0.67$, $H^\circ_{0,h.i.rot}/T = 0.75$, and $(C^\circ_p)_{h.i.rot} = 1.65$.

15.3.2. Vibrational Partition Function

We shall consider that a molecule consists of independent harmonic oscillators.

It is known from quantum mechanics that

$$\varepsilon_{vib} = (\varepsilon_0)_{vib} + (\varepsilon_i)_{vib} = \left(v + \frac{1}{2}\right) h\nu \qquad (15.45)$$

where v = vibrational quantum number acquiring values of 0, 1, 2, ...
h = Planck constant
ν = frequency of vibrations.*

* With anharmonicity (very high temperatures), this equation becomes

$$\varepsilon_{vib} = \left(v + \frac{1}{2}\right) h\nu - \left(v + \frac{1}{2}\right) \chi h\nu - \ldots$$

where χ is the anharmonicity constant.

The second term of the right-hand side of the equation shows that even in the lowest vibrational state ($T = 0$) a **zero vibrational energy** remains $\left(\frac{1}{2}h\nu\right)$ which is usually included in the zero energy U_0°.

For all the vibrational levels of most molecules, we have $g_{vib} = 1$. Therefore in accordance with Eq. (15.3) for a two-dimensional oscillator (a diatomic molecule), the partition function of the vibrational energy exceeding the zero energy is

$$Q_{vib} = \exp\left[-\frac{\left(0+\frac{1}{2}\right)h\nu}{kT}\right] + \exp\left[-\frac{\left(1+\frac{1}{2}\right)h\nu}{kT}\right] + \exp\left[-\frac{\left(2+\frac{1}{2}\right)h\nu}{kT}\right] + \ldots$$

$$\ldots = \left[1 + \exp\left(-\frac{h\nu}{kT}\right) + \exp\left(-\frac{2h\nu}{kT}\right) + \ldots\right] \times \exp\left(-\frac{h\nu}{2kT}\right) = \left[1 - \exp\left(-\frac{h\nu}{kT}\right)\right]^{-1} = \left[1 - \exp\left(-\frac{\Theta}{T}\right)\right]^{-1} \qquad (15.46)^*$$

where Θ is the characteristic temperature (see p. 63).

For polyatomic molecules

$$Q_{vib} = \left[1 - \exp\left(-\frac{h\nu_1}{kT}\right)\right]^{-1}\left[1 - \exp\left(-\frac{h\nu_2}{kT}\right)\right]^{-1} \ldots \qquad (15.47)$$

where ν_1, ν_2, ... are the characteristic frequencies of the various vibrations in a given molecule.

Combining Eq. (15.47) with Eqs. (15.20)-(15.23), we get

$$(U^\circ - H_0^\circ)_{vib} = (H^\circ - H_0^\circ)_{vib} = RT\sum^{i}\frac{\Theta/T}{e^{\Theta/T} - 1} \qquad (15.48)$$

$$(C_V^\circ)_{vib} = (C_p^\circ)_{vib} = R\sum^{i}\frac{e^{\Theta/T}(\Theta/T)^2}{(e^{\Theta/T} - 1)^2} \qquad (15.49)^{**}$$

$$S_{vib}^\circ = R\sum^{i}\left[\frac{\Theta/T}{e^{\Theta/T} - 1} - \ln\left(1 - e^{-\Theta/T}\right)\right] \qquad (15.50)$$

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* When $x \ll 1$, we have $1 + x + x_2 + \ldots = 1/(1 - x)$.

** When $i = 3$, Eq. (15.49) coincides with Eq. (3.15).

and

$$\left(\frac{G^\circ - H_0^\circ}{T}\right)_{vib} = R \sum^{i} \ln (1 - e^{-\Theta/T}) \qquad (15.51)^*$$

Summation for polyatomic linear molecules covers $3n - 5$ vibrations, and for polyatomic non-linear molecules $3n - 6$ vibrations, where n is the number of atoms in a molecule. The frequencies of vibrations ν are usually replaced with the **wave numbers** (quantities that are reciprocals of the wavelength λ) for convenience. Since $\Theta = h\nu/k = (hc/k)(1/\lambda)$, the following factor serves for recalculation:

$$\frac{hc}{k} = \frac{(6.626\,176 \times 10^{-27})(2.997\,76 \times 10^{10})}{1.380\,662 \times 10^{-16}} = 1.4374 \text{ cm} \cdot \text{K}$$

here c is the velocity of light.

Calculations are facilitated by tables giving the properties due to vibrational degrees of freedom (see, for example, Appendix 5, which gives the values of the properties per degree of freedom).

When there are internal rotations, the number of factors in Eq (15.47) decreases by n, where n is the number of free or hindered rotations (or the number of rotational vibrations) of separate groups of molecules. The right-hand sides of Eqs. (15.48)-(15.51) will change accordingly.

To take into consideration the anharmonicity of vibrations and the influence of vibrations on the rotational levels, the corresponding equations were proposed and corrections to Eq. (15.46) were calculated. Tables were also compiled that permit us to directly find $C^\circ_{vib\text{-}rot}$, $S^\circ_{vib\text{-}rot}$ and $[(G^\circ - H_0^\circ)/T]_{vib\text{-}rot}$.

In these tables (see, for example, [D47]), the corresponding quantities are given as functions of Θ/T and the anharmonicity constant χ.

Example 5. Find the value of S°_{vib} for C_2H_4 at $t = 25\,^\circ C$ using the values of Θ given below.

Solution. The quantity $\Sigma(S^\circ_{vib})_{298}$ can be calculated either by Eq. (15.50) or by using the data of Appendix 5. To save time, we

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* Equations (15.48)-(15.51) are obtained from Eqs. (15.20)-(15.23) on the grounds that

$$\frac{d \ln Q_{vib}}{d \ln T} = \frac{\Theta/T}{e^{\Theta/T} - 1} \quad \text{and}$$

$$\frac{d^2 \ln Q_{vib}}{d(\ln T)^2} = \frac{(\Theta/T)^2 e^{\Theta/T}}{(e^{\Theta/T} - 1)^2} - \frac{\Theta/T}{e^{\Theta/T} - 1}$$

shall choose the second way. This gives us the following results:

Θ	$\frac{\Theta}{298.15}$	$(S_i^\circ)_{vib}$	Θ	$\frac{\Theta}{298.15}$	$(S_i^\circ)_{vib}$
1186	3.977	0.189	2076	6.962	0.015
1350	4.527	0.123	2333	7.825	0.007
1366	4.581	0.115	4295	14.404	0.000
1366	4.581	0.115	4340	14.555	0.000
1581	5.302	0.063	4412	14.797	0.000
1929	6.469	0.023	4461	14.961	0.000

Summation of the values of $(S_i^\circ)_{vib}$ yields $\sum(S_i^\circ)_{vib} = 0.650$.

Example 6. Find C_p° for CH_4 within the interval from 300 to 1500 K (by steps of 200 K). Take the values of Θ from Appendix 7.

Solution. In accordance with Eqs. (15.9) and (15.40), we have

$$C_p^\circ = 7.949 + \sum C_{vib}^\circ$$

Using the values of Θ found from Appendix 7 and the data of Appendix 5, we calculate the values of $\sum C_{vib}^\circ$:

Θ	1870 (3)	2170 (2)	4320 (3)	4400	
$T = 300$; Θ/T	6.233	7.233	14.400	14.667	
$(C_{vib}^\circ)_i$	$3 \times 0.154 + 2 \times 0.075 + 3 \times 0.000 + 0.000$				$= 0.612$
$T = 500$; Θ/T	3.740	4.340	8.640	8.800	
$(C_{vib}^\circ)_i$	$3 \times 0.693 + 2 \times 0.501 + 3 \times 0.027 + 0.023$				$= 3.185$
$T = 700$; Θ/T	2.671	3.100	6.171	6.286	
$(C_{vib}^\circ)_i$	$3 \times 1.132 + 2 \times 0.943 + 3 \times 0.160 + 0.148$				$= 5.590$
$T = 900$; Θ/T	2.078	2.522	4.800	4.889	
$(C_{vib}^\circ)_i$	$3 \times 1.403 + 2 \times 1.201 + 3 \times 0.383 + 0.361$				$= 8.121$
$T = 1100$; Θ/T	1.700	1.973	3.927	4.000	
$(C_{vib}^\circ)_i$	$3 \times 1.570 + 2 \times 1.452 + 3 \times 0.628 + 0.604$				$= 10.102$
$T = 1300$; Θ/T	1.438	1.670	3.323	3.384	
$(C_{vib}^\circ)_i$	$3 \times 1.678 + 2 \times 1.584 + 3 \times 0.851 + 0.826$				$= 11.581$
$T = 1500$; Θ/T	1.247	1.446	2.880	2.933	
$(C_{vib}^\circ)_i$	$3 \times 1.748 + 2 \times 1.675 + 3 \times 1.039 + 1.016$				$= 12.727$

The values of the heat capacities are given below:

T	300	500	700	900	1100	1300	1500
C_p°	8.561	11.134	13.539	16.070	18.051	19.530	20.776

It follows from the data obtained that the levels $\Theta = 4320$ and 4400 are excited only at high temperatures.

A comparison of the results obtained with experimental data gives a deviation less than 0.2% for the region of low temperatures, where the values of C_p° calculated from experimental data are most reliable.

15.3.3. Partition Function for Electronic Excitation

The statistical weight of each electronic level $g_e = 2j + 1$. Therefore in accordance with Eq. (15.3), we have

$$Q_e = (2j_0 + 1) + (2j_1 + 1)\exp\left(-\frac{\varepsilon_1}{kT}\right) + \\ + (2j_2 + 1)\exp\left(-\frac{\varepsilon_2}{kT}\right) + \ldots \qquad (15.52)$$

where j_i is the quantum number of the levels of energy of the electrons, equal to the orbital quantum number plus the resultant spin of the electrons.

Equations (15.20)-(15.23) with Q_e substituted in them for Q are used to calculate $(U^\circ - H_0^\circ)_e = (H^\circ - H_0^\circ)_e$, C_e°, S_e° and $[(G^\circ - H_0^\circ)/T]_e$.

The electronic levels as a rule correspond to a very great energy, i.e. only a negligible fraction of the molecules is in an excited state (the influence of the second term is noticeable only when $T > h\nu/4k$). Other levels have to be taken into account in addition to the ground level only at very high temperatures, when optical excitation of the molecules occurs. Even in this case, however, we may limit ourselves to two or three terms of Q_e.

Consequently, owing to the absence of multiplet electronic levels in the majority of polyatomic gases (exceptions are Cl_2, O_2, NO and certain other gases at $T > 2000$ K), we can conclude that $j = 0$, $g_e = 1$ and $Q_e = 1$.

The data needed for the calculations are given in Table 27.

Table 27. **Statistical Weights and Wave Numbers for Atoms of Selected Elements in the State of a Monoatomic Ideal Gas**

Element	Lower (ground) level		Higher levels					
	Term *	Statistical weight	Term *	Statistical weight	$\tilde{\nu}$, cm^{-1}	Term *	Statistical weight	$\tilde{\nu}$, cm^{-1}
Br	$^2P_{3/2}$	4	$^2P_{1/2}$	2	3 685	$^4P_{5/2}$	6	63 430
C	$^3P_0$	1	$^3P_1$	3	148	^1P	5	10 192
Cl	$^3P_{3/2}$	4	$^2P_{1/2}$	2	881	$^4P_{5/2}$	6	71 954
F	$^2S_{3/2}$	4	$^2P_{1/2}$	2	407	$^4P_{5/2}$	6	102 412
H	$^2S_{1/2}$	2	—	—	82 258.3	—	—	97 481.4

Table 27 (concluded)

Element	Lower (ground) level		Higher levels					
	Term*	Statistical weight	Term*	Statistical weight	$\tilde{\nu}$, cm^{-1}	Term*	Statistical weight	$\tilde{\nu}$, cm^{-1}
I	$^2P_{3/2}$	4	$^2P_{1/2}$	2	7 680	$^2P_2$	5	42.3
N	$^4P_{3/2}$	4	—	—	>27 400	—	5	—
O	$^3P_2$	5	$^3P_1$	3	158	$^3P_0$	1	227
P	$^4S_{3/2}$	4	—	—	15 700	—	—	—
S	$^3P_2$	5	$^2P_1$	3	398	$^3P_0$	1	572

* The symbol in the term stands for the state of the atom: S at $L=0$, P at $L=1$, D at $L=2,\ldots$, where L is the orbital quantum number (the resultant vector of the moments of orbital motion of the electrons), which takes on integral values in units of $h/2\pi$. The superscript, equal to $2s_e+1$, stands for the multiplicity (the number of sublevels due to spin of the electrons; s_e is the resultant vector of the moments of the spins, acquiring values of 0, 1, 2,... with an even number of electrons, and 1/2, 3/2, 5/2,... with an odd number). The subscript equals the quantum number j.

15.3.4. Nuclear Spin

When nuclear spin occurs, a factor taking into account its influence on the rotational levels must be introduced in Eqs. (15.28)-(15.34). If we assume that Q_{rot} and Q_{nuc} are independent of each other, we get

$$Q_{rot\text{-}nuc} \approx Q_{rot}Q_{nuc} = Q_{rot}(2s_1 + 1)(2s_2 + 1)\ldots \qquad (15.53)$$

where s_i is the spin quantum number.

The number of multipliers of the form $(2s_i + 1)$ in Eq. (15.53) equals the number of atoms in a molecule.

The spin of a nucleus equals the sum of the spins of the particles which form it. Therefore, if the sum of the protons and neutrons is an even number, the spin equals an integer (or zero); otherwise the spin is a half-integer. The values of the spin quantum numbers for selected elements are given below:

Element	C, He, O	F, H, P	D, N	As, Na	Cl
s	0	$\frac{1}{2}$	1	$\frac{3}{2}$	$\frac{5}{2}$

Since $Q_{nuc} \neq \varphi(T)$, the spin, as follows from Eqs. (15.20) and (15.21), does not influence H°, C_V° and C_p°, but in accordance with Eqs. (15.22) and (15.23) it does change the entropy and Gibbs energy. In this connection, complete (absolute or spectroscopic) and practical (thermochemical) entropies are distinguished. The latter equals the total entropy less the "spin entropy", i.e.

$$S^\circ_{pract} = S^\circ_{abs} - R\sum \ln (2s + 1) \qquad (15.54)$$

We may consider that every atom has an identical spin regardless of whether it is in the isolated state or is a part of a compound.

Therefore, in calculating $\Delta S°$ and $\Delta G°$ and, consequently, in calculating equilibrium, the spin components mutually eliminate each other. Nuclear spin must be taken into account only for very low temperatures (for hydrogen below 0 °C, for deuterium below 70 °C, for other substances at still lower temperatures).

15.3.5. Effect of Isotopic Composition

The presence of isotopes causes only the equations including mass, moments of inertia and frequencies of vibrations to change. Hence isotopes do not affect the energies and enthalpies (counted from absolute zero), and also the heat capacities. The entropy and Gibbs energy for a mixture of isotopes will be different, because the mixing of isotopes results in changes in the entropy $S°_{\text{isot}} = R\sum x_i \ln x_i$ and the function of the Gibbs energy $[(G° - H°_0)/T]_{\text{isot}} = -R\sum x_i \ln x_i$ that are independent of the temperature.

In an approximate method of calculations, we can use the "averaged" values of the atomic weights instead of taking into account the effect of isotopic composition. Since the entropy of mixing is constant for each mole of atoms both in the reactants and the products, it drops out of the calculations. This effect must be taken into consideration only in calculating processes of separation and redistribution of isotopes.

15.3.6. Group of Properties

When calculating the properties of a monoatomic gas, we must take Q_{trans} and Q_e into consideration. For polyatomic gases, we have to use the expression for Q containing all the multipliers. As indicated above, however, in the majority of cases we may ignore the electronic component and the nuclear spin, i.e. take account only of Q_{trans}, Q_{rot} and Q_{vib}.

To use the properties of ideal gases found in this way for determining the properties of real gases, we must use, as also indicated above, the corresponding equations (see Chap. 6). We can find the properties of substances in the liquid and solid states if we have at hand the values of the heats of phase transitions and heat capacities.

We must note once more that only approximate calculations can be performed for complex molecules. A source of possible errors may be the usual method of determining the magnitude of the energy barrier by comparing the summary entropy or Gibbs energy with the results of calculations based on experimental data. In addition, it is impossible to take accurate account of the internal rotation in molecules with long chains. In such cases, it is more reliable to

extrapolate the values of the properties of lower homologues with the aid of the data given in Appendix 3. The frequencies of vibrations sometimes have to be chosen so that the entropies, heat capacities and Gibbs energies found on their basis will be close to those obtained by direct measurement.

Example 7. Use the data given in Table 27 and in Sec. 15.3.4 to find the partition function for atomic oxygen at 298, 1000, 2000, 3000, 4000 and 5000 K. Assess the part of the metastable levels (not indicated in Table 27) consisting of the terms $^1D_2$ ($g = 5$) and $^1S_0$ ($g = 1$) with frequencies of vibrations of 15 807 and 33 662 cm^{-1}, respectively.

Solution. The spin of the nucleus of an oxygen atom equals zero. Therefore $Q_{spin} = 1$ and $Q = Q_e$. Hence in accordance with the data of Table 27 and Eq. (15.3), we get (per g-atom)

$$Q = 5 + 3e^{-227.8/T} + e^{-320.4/T} + 5e^{-22\,700/T} + e^{-48\,405/T}$$

The numerators of the exponents have been found by multiplying the relevant frequencies by $hc/k = 1.4374$ (see p. 585).

Inspection of the results given below shows that the last two levels may be omitted from the calculations, because their part in the value of Q at $T < 3000$ is less than 0.04%.

Energy above zero energy, cal/g-atom		0		451.6		648.8		45 159		96 205	
$g_i e^{-\varepsilon_i/RT}$	=	$g_0 e^{-0/RT}$	+	$g_1 e^{-\varepsilon_1/RT}$	+	$g_2 e^{-\varepsilon_2/RT}$	+	$g_3 e^{-\varepsilon/RT}$	+	$g_4 e^{-\varepsilon_4/RT}$	= $\Sigma g_i e^{-\varepsilon_i/RT}$
$Q_{298.2}$	=	5	+	1.400	+	0.335	+	10^{-33}	+	10^{-71}	= 6.735
Q_{1000}	=	5	+	2.390	+	0.722	+	10^{-9}	+	10^{-21}	= 8.112
Q_{2000}	=	5	+	2.684	+	0.849	+	0.000	+	10^{-11}	= 8.533
Q_{3000}	=	5	+	2.781	+	0.896	+	0.003	+	10^{-8}	= 8.680
Q_{4000}	=	5	+	2.834	+	0.922	+	0.017	+	10^{-5}	= 8.773
Q_{5000}	=	5	+	2.866	+	0.937	+	0.053	+	10^{-4}	= 8.856

Example 8. Use the results of the preceding example to find the properties of atomic oxygen at $T = 298.15$ K.

Solution. By Eqs. (15.6) and (15.20) we have

$$(U^\circ - U_0^\circ)_{298} = (U^\circ_{trans})_{298} + (U^\circ_e)_{293} = 2.981 \times 298.2 +$$

$$+ \frac{451.6 \times 1.400 + 648.8 \times 0.335}{6.735} = 882.9 + 125.8 = 1008.7$$

From Eqs. (15.8) and (15.20) in accordance with the above, we get

$$(H^\circ - U_0^\circ)_{298} = (H^\circ_{trans})_{298} + (H^\circ_e)_{298} = 4.968 \times 298.15 + 125.8 = 1607.2$$

If we relate the energy to one g-atom, then by Eqs. (15.7) and (15.21)

$$(C_V^\circ)_{298}=2.981+\frac{1}{1.987\times 298.2^2}\times\left[\frac{451.6^2\times 1.400+648.8^2\times 0.335}{6.735}-\right.$$

$$\left.-\left(\frac{451.6\times 1.400+648.8\times 0.335}{6.735}\right)^2\right]=2.981+\frac{63\,058-15\,832}{176\,692}=$$

$$=2.981+0.267=3.248\ \text{cal/mol}\cdot\text{K}$$

By Eqs. (15.9) and (15.21) in accordance with the above, we have $(C_p^\circ)_{298}=4.968+0.267=5.235$.

Since the equations for C_V° and C_p° include terms containing ε^2, the level $^1D_2$ must be taken into consideration when calculating the heat capacity already at $T>1000$ K.

By Eqs. (15.12) and (15.22) we obtain

$$S_{298}^\circ=(S_{\text{trans}}^\circ)_{298}+(S_e^\circ)_{298}=(6.8635\log 16+25.991)+$$

$$+4.5756\log 6.735\,\frac{451.6\times 1.400+648.8\times 0.335}{298.2\times 6.735}=$$

$$=34.256+4.207=38.463\ \text{cal/mol}\cdot\text{K}$$

By Eqs. (15.18) and (15.23)

$$[(G^\circ-H_0^\circ)/T]_{298}=-6.8635\log 16-11.4391\log 298.2-$$

$$-4.5756\log 6.735+7.282=-8.265-28.306-3.790+$$

$$+7.282=-33.079\ \text{cal/mol}\cdot\text{K}$$

Example 9. Calculate the standard entropy of ethene without and with account taken of the nuclear spin effect.

Solution. The standard entropy of ethene will consist of S_{trans}°, S_{rot}° and S_{vib}°. Taking the corresponding quantities from the solutions of Examples 1, 3 and 5, we get

$$S_{298}^\circ=36.02+15.80+0.65=52.47$$

The found value completely agrees with the values of 52.48 ± 0.1 and 52.45 ± 0.10 obtained in recalculating the "thermochemical" entropies for the standard state.

The total entropy of ethene, i.e. S_{298}°, taking into account the hydrogen nuclei spin effect in accordance with Eq. (15.54) and with $s_H=\frac{1}{2}$ (see Sec. 15.3.4) will be

$$S_{298}^\circ=52.47+4R\ln\left(2\times\frac{1}{2}+1\right)=52.47+4\times 1.377=57.98\ \text{e.u.}$$

15.4. CALCULATION OF CHEMICAL EQUILIBRIUM

Denoting by $\Delta U_0^\circ = \Delta H_0^\circ$ the change in energy (enthalpy) for a hypothetical standard reaction proceeding at $p = 1$ atm and absolute zero, we can write down that

$$\Delta G^\circ = \Delta G^\circ - \Delta H_0^\circ + \Delta H_0^\circ \qquad \text{or}$$

$$\frac{\Delta G^\circ}{T} = \Delta\left(\frac{G^\circ - H_0^\circ}{T}\right) + \frac{\Delta H_0^\circ}{T}$$

whence in combination with Eq. (14.8) we get

$$R \ln K_p = -\left[\Delta\left(\frac{G^\circ - H_0^\circ}{T}\right) + \frac{\Delta H_0^\circ}{T}\right] \tag{15.55}$$

A glance at this equation shows that the quantities $(G^\circ - H_0^\circ)/T$ for all the reagents and the hypothetical heat effect ΔH_0° for the reaction of the gaseous reagents at absolute zero must be known to calculate the equilibrium constant.

The values of $-(G^\circ - H_0^\circ)/T$ are determined on the basis of spectroscopic data according to the relevant equations of the preceding sections and the data of Table 28. More extensive tables are given in reference books. For hydrocarbons they are contained in [B115].

Before calculating the values of ΔH_0° (they are also given in Table 28), we shall indicate the following. It is impossible to determine the values of H_0° including the zero, electronic and vibrational levels for the molecules of one species, but this is not significant, because H_0° drops out of the final results of the calculations. For a chemical reaction, H_0° transforms into ΔH_0°, which is simple to determine.

There are several ways to determine ΔH_0°.

1. By using tables of the function $-(G^\circ - H_0^\circ)/T$ for all the reagents:

(a) if we know one value of K_p (or ΔG_T°) — by Eq. (15.55);

(b) if we know the values of ΔH_T° and ΔS_T° for all the reagents — by the equation

$$\Delta H_0^\circ = T\left[\Delta\left(-\frac{G^\circ - H_0^\circ}{T}\right) - \Delta S_T^\circ\right] + \Delta H_T^\circ \tag{15.56}$$

which is obtained by combining Eq. (15.55) with Eqs. (13.8) and (13.71).

2. By using values of $H_T^\circ - H_0^\circ$ for each of the reagents by Eqs. (15.23) and (15.35) or (15.39) and (15.48) in combination with the heats of the reaction ΔH_T° with the aid of Eq. (13.76). The calcu-

Table 28. **Values of $-(G^\circ - H_0^\circ)/T$ and ΔH_0° for Graphite and Selected Gases ***

Substance	$-(G^\circ - H_0^\circ)/T$ at T, K							ΔH_0°, kcal/mol
	298.15	400	600	800	1000	1200	1500	
C	0.5172	0.8245	1.477	2.138	2.771	3.365	4.181	0
Cl_2	45.951	48.148	51.297	53.614	55.453	56.979	58.870	0
H_2	24.423	26.422	29.203	31.186	32.738	34.012	35.590	0
N_2	38.817	40.861	43.688	45.711	47.306	48.629	50.284	0
O_2	42.081	44.104	46.964	49.044	50.697	52.079	53.810	0
S_2	47.242	49.379	52.437	54.688	56.479	—	59.823	0
CO	40.350	42.393	45.222	47.254	48.860	50.196	51.884	−27.18
CO_2	43.555	45.828	49.238	51.895	54.109	56.019	58.461	−93.949
COS	47.39	49.81	53.50	55.37	58.75	60.79	63.40	−22.2
CS_2	48.28	50.90	54.89	57.97	60.51	62.57	65.44	−3.6
HCl	37.734	39.771	42.588	44.597	46.171	47.472	49.096	−21.984
H_2O	37.172	39.508	42.768	45.131	47.018	48.605	50.622	−57.108
H_2S	41.174	43.53	46.83	49.27	51.24	52.92	55.06	−19.62
NH_3	37.989	40.380	43.826	46.450	48.634	—	53.033	—
NO	42.985	45.141	48.100	50.214	51.878	53.259	54.979	21.579
SO_2	50.95	53.49	57.21	60.05	62.39	64.37	66.91	−85.86
SO_3	51.94	54.81	59.31	62.98	66.12	68.87	—	−22.7
CH_4	36.46	38.86	42.39	45.21	47.65	49.86	52.84	−15.96
C_2H_2	40.01	42.29	46.38	49.50	52.14	—	57.43	53.44
C_2H_4	44.05	46.7	50.8	54.4	57.5	—	64.2	14.51
C_2H_6	45.25	48.20	53.06	57.28	61.12	—	69.49	−16.48
C_3H_6	54.3	57.6	63.3	68.3	72.9	—	82.8	8.58
C_3H_8	52.83	56.62	63.13	69.00	74.44	—	86.3	−19.44
C_4H_8 (butene-1)	62.0	66.3	73.9	80.6	86.8	—	100.3	5.49
iso-C_4H_8	57.0	61.6	69.4	76.3	82.5	—	95.9	—
C_4H_8 (*cis*-butene-2)	60.0	64.3	71.7	78.4	84.4	—	97.5	3.65
C_4H_8 (*trans*-butene-2)	59.4	63.7	71.1	77.8	83.8	—	96.9	2.70
C_4H_{10}	58.54	63.56	72.16	79.93	87.12	—	102.65	−23.25
iso-C_4H_{10}	56.14	60.85	69.21	70.90	83.99	—	99.54	−24.52
C_5H_{12}	64.19	70.32	80.89	90.51	99.37	—	118.49	−27.03
iso-C_5H_{12}	64.70	70.40	80.63	90.12	98.87	—	118.01	−28.45
neo-C_5H_{12}	56.28	61.87	72.18	81.71	90.55	—	109.96	−31.07
C_6H_6	52.98	56.75	63.81	70.42	76.66	—	90.60	—
C_6H_{14}	69.86	77.12	89.69	101.15	111.68	—	134.40	−31.05

* More complete tables covering a greater temperature interval can be found, for example, in [B114].

lations are usually performed for $T = 298.15$ K. The values of $H^\circ - H_0^\circ$ for selected substances are given in Table 29.

3. According to high-temperature calorimetric quantities in combination with spectroscopic data by the equation

$$\Delta H_0^\circ = \Delta H^\circ - \Delta\left(RT\frac{d\ln Q_{in}}{d\ln T} + \frac{5}{2}RT\right) \qquad (15.57)$$

obtained from Eqs. (15.20) and (15.8) for each of the reagents.

4. According to spectroscopic data if the different states of excitation of a molecule are known up to its dissociation into atoms.

5. By combining the values of ΔH_0° for other reactions.

The values of $H^\circ - H_0^\circ$ and $(G^\circ - H_0^\circ)/T$ found by spectroscopic means are highly accurate, whereas the values found from calorimetric measurements of the heats of reactions (according to the heats of combustion or formation) are not always sufficiently accurate. This is a possible reason for the lack of authenticity of ΔH_0°.

It must be noted that the relevant tables sometimes give non-uniform data, i.e. for some reagents the values $-(G^\circ - H_0^\circ)/T$ are given taking nuclear spin into account, and for others without taking it into account. In such cases, uniform values must be obtained for all the substances before starting to calculate equilibrium. Thus, if for a substance containing hydrogen (for instance for a hydrocarbon), the values of $-(G^\circ - H_0^\circ)/T$ are given taking nuclear spin into account, then to exclude it, the quantity $R\ln 2$ must be subtracted from the value of $-(G^\circ - H_0^\circ)/T$ for each hydrogen atom in accordance with Eq. (15.54) and the data of Sec. 15.3.4.

Example 10. Find the equilibrium constant for the reaction

$$C_3H_6 + H_2 = C_3H_8$$

at $t = 327\,^\circ$C and compare it with the value of $\log K_p = 3.79$ found by studying equilibrium experimentally.

Solution. Using the data of Table 28, we find

$$\Delta H_0^\circ = (\Delta H_0^\circ)_{C_3H_8} - [(\Delta H_0^\circ)_{C_3H_6} + (\Delta H_0^\circ)_{H_2}] =$$

$$= -19\,440 - (8580 + 0) = -28\,020 \text{ cal/mol}$$

From Table 28 for $T = 600$ K we have

$$\Delta\left(\frac{G^\circ - H_0^\circ}{T}\right) = \left(\frac{G^\circ - H_0^\circ}{T}\right)_{C_3H_8} -$$

$$-\left[\left(\frac{G^\circ - H_0^\circ}{T}\right)_{C_3H_6} + \left(\frac{G^\circ - H_0^\circ}{T}\right)_{H_2}\right] =$$

$$= -63.13 - [(-63.3) + (-29.203)] = 29.373 \text{ cal/mol}\cdot\text{K}$$

Table 29. **Values of $H^\circ - H_0^\circ$ (in kcal/mol) for Graphite and Selected Gases**

Substance	$(H^c - H_0^\circ)$ at T, K					
	298.15	400	600	800	1000	1500
C	0.252	0.503	1.198	2.082	3.075	5.814
H_2	2.023	2.731	4.129	5.537	6.966	10.694
N_2	2.072	2.782	4.198	5.669	7.203	11.254
O_2	2.070	2.792	4.279	5.854	7.497	11.776
CO	2.073	2.784	4.210	5.700	7.257	11.359
CO_2	2.238	3.195	5.322	7.689	10.222	17.004
H_2O	2.365	3.190	4.873	6.666	8.580	13.876
H_2S	2.386	3.22	4.99	6.92	9.01	14.79
NH_3	2·407	3.299	5.266	7.572	10.123	17.460
NO	2.206	2.923	4.385	5.834	7.584	11.701
SO_2	2.53	3.53	5.75	8.17	10.70	17.29
SO_3	2.77	4.10	7.22	10.78	14.63	—
CH_4	2.397	3.323	5.549	8.321	11.560	21.130
C_2H_2	2.392	3.54	6.13	11.33	12.09	20.54
C_2H_4	2.59	4.75	10.15	16.87	24.64	—
C_2H_6	2.865	4.27	8.03	12.78	18.37	34.56
C_3H_6	3.20	6.36	14.49	24.75	36.62	—
C_3H_8	3.535	5.59	11.06	17.91	25.92	48.77
C_4H_6	3.64	5.84	11.51	18.41	26.16	45.87
1-C_4H_8	4.22	6.69	13.01	20.86	29.83	55.59
iso-C_4H_8	4.06	6.52	12.75	20.50	29.37	55.01
cis-2-C_4H_8	3.94	6.14	12.01	19.51	28.23	53.61
trans-2-C_4H_8	4.19	6.58	12.70	20.35	29.19	54.71
C_4H_{10}	4.66	7.43	14.63	23.68	34.13	63.74
iso-C_4H_{10}	4.29	7.08	14.39	23.50	34.00	64.00
C_5H_{12}	5.68	9.12	18.04	29.21	42.08	78.42
iso-C_5H_{12}	5.17	8.63	17.70	28.98	41.91	78.69
neo-C_5H_{12}	5.05	8.56	17.81	29.37	42.54	79.50
C_6H_6	3.325	5.76	12.29	20.61	30.16	57.36
C_6H_{14}	6.71	10.83	21.46	34.76	50.04	93.10
C_6H_{14}, methylpentane	5.96	10.1	20.5	33.6	48.7	75.09
C_7H_{16}	7.71	12.41	23.86	39.59	56.89	101.9

By Eq. (15.55)

$$R \ln K_p = -\left[29.373 + \left(-\frac{28\,020}{600}\right)\right] = 17.327$$

whence $\log K_p = 17.327/4.5756 = 3.787$. The calculations confirm the authenticity of the experimental data.

Example 11. Use the data of Tables 28 and 29 to find the standard heat effect of the hydrogenation of propene.

Solution. According to Hess's law, we have

$$\Delta H_T^\circ = \Sigma[(H_T^\circ - H_0^\circ) + \Delta H_0^\circ]_{pr} - \Sigma[(H_T^\circ - H_0^\circ) + \Delta H_0^\circ]_r$$

Using the data of Tables 28 and 29, we get for the reaction of hydrogenation of propene

$$\Delta H_{298}^\circ = [(H_{298}^\circ - H_0^\circ)_{C_3H_6} + (\Delta H_0^\circ)_{C_3H_6}] -$$

$$- \{[(H_{298}^\circ - H_0^\circ)_{C_3H_6} + (\Delta H_0^\circ)_{C_3H_6}] + [(H_{298}^\circ - H_0^\circ)_{H_2} + (\Delta H_0^\circ)_{H_2}]\} =$$

$$= [3.535 + (-19.44)] - [(3.20 + 8.58) + (2.023 + 0)] =$$

$$= -29.708 \text{ kcal/mol}$$

The directly measured heat of hydrogenation ΔH_{355} was used to find $\Delta H_{298} = -29.800$ cal/mol [D47] which differs from the results of the calculations by a value that is within the permissible errors of experiments and calculations.

Example 12. Find the composition of the equilibrium mixture obtained in the isomerization of pentane with the aid of the data of Table 28. Perform the calculations for the interval of 300 to 1000 K at steps of 100 K. At what temperatures should the process be conducted to achieve the maximum yield of the isopentane?

Solution. We perform the calculations for $T = 400$ K. Using the data of Table 28, by Eq. (15.55) we get $K_p = 1$ for pentane, $K_p = 6.21$ for isopentane and $K_p = 2.30$ for neopentane.

Next we determine the composition of the mixture:

C_5H_{12}	1.0 mol = 10.5%
iso-C_5H_{12}	6.21 mol = 65.4%
neo-C_5H_{12}	2.30 mol = 24.1%
	9.51 mol = 100%

After performing similar calculations for the other temperatures, we get the results shown in Fig. 195. Examination of this figure shows that a temperature of about 500 K should be maintained in the reaction zone to achieve the maximum yield of isopentane. At this temperature, the equilibrium mixture should contain about 69% of isopentane.

The results of our calculations confirm the law noted on p. 522 — the predominance of normal hydrocarbons over their isomers in the products of petroleum refining.

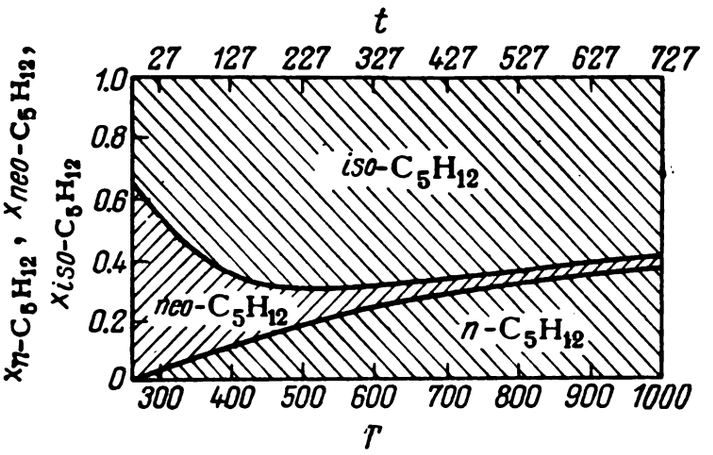


Fig. 195. Temperature dependence of equilibrium composition in the isomerization of pentane.
(See Example 12)

It can be seen from the above that the merits of the statistical method of calculating thermodynamic properties and chemical equilibrium are so great that it should be preferred to any other method when the accurate data needed for the calculations are available and the difficulties involved can be surmounted. Numerous equations and tables greatly facilitate many stages of the calculations.

The statistical method allows us to take into consideration effects that do not lend themselves to treatment by the methods of classical thermodynamics (nuclear spin, the effect of isotopic composition, etc.).

The spectroscopic method makes it possible to find authentic values of the heat capacities and enthalpies of substances (and according to them, the heat effects of reactions). This is especially important when thermodynamic data are insufficiently reliable or are not available. In the latter case, the unknown quantity (for example the heat capacity) is usually replaced by the value of a substance close in its properties to the one in question. Such a procedure cannot naturally give accurate results. It is therefore natural that in compiling Tables 1, 4, 14, 18 and Appendix 2 preference was given to spectroscopic data when they were available.

The statistical method, unlike the calorimetric one, can be used to get accurate data for temperatures that are virtually unobtainable. It can be applied for such particles which cannot be separated, but which play an important part in high-temperature gas reactions

(OH, SO, etc.). The explanation is that free radicals do not have time to disappear during the act of emission (or absorption) of light, and their spectra can be registered.

It is very simple to calculate chemical equilibrium by the statistical method, and the results are highly accurate, because the main cause of the errors in calculating by the methods treated in Chap. 13 — the lack of authenticity of the heat effects (especially of the values of the heats of formation of compounds from simple substances) — no longer exists. In the few cases when the heat effects are sufficiently reliable, spectroscopic calculations nevertheless permit us to obtain more accurate results, because they exclude the inaccuracy of the temperature dependence of the heat capacity.

The significance of this method should not be exaggerated, however. It is faultless theoretically, but when used in practice for complex gaseous molecules, as well as for solids and liquids, it almost always has to be combined with thermal methods. Inaccuracies in the configuration of a molecule, the interatomic distances and valence angles in it, the unauthenticity of assigning the frequencies are a far from complete list of the factors reducing the reliability of the results because of an indefiniteness of the initial quantities and their interpretation.

Appendices

APPENDIX 1

LIST OF SYMBOLS*

The units given below for some of the quantities have often been omitted in the text, especially in the figures. (If other units are used, they are always indicated.) Thus, a definite quantity is always measured in the same units. For example p and T correspond to the absolute pressure in physical atmospheres and the temperature in kelvins. Extensive quantities are expressed in units per mole. For example the units of V and S are cm^3/mol and cal/mol·K, respectively. When instead of molar quantities, the extensive properties are considered regardless of the amount of a substance, no new units are introduced, but it is understood that the given quantity corresponds to the total amount of a substance (this is often specially indicated).

A	atomic mass; constant; Helmholtz energy (cal/mol); parameter
A_S	area (cm^2)
$-\Delta A_T$	maximum work (cal/mol)
a	activity; constant
B	coefficient; constant; magnetic induction; parameter
b	constant
C	coefficient; constant; heat capacity (cal/mol·K)
c	coefficient; concentration (molar-volume); velocity of light (cm/s)
D	coefficient; relative permittivity (dielectric constant)
d	coefficient
E	electromotive force (e.m.f.) (V); energy (cal/mol)
El	element

* In the English translation of this book, the recommendations contained in the Manual of Symbols and Terminology for Physicochemical Quantities and Units adopted by the IUPAC Council at Cortina d'Ampezzo, Italy, on July 7, 1969 (see *Pure and Applied Chemistry*, Vol. 21, No. 1, 1970) have been used wherever possible. — *Translator's note.*

e	base of natural logarithms; charge of an electron
F	Faraday constant; force
f	activity coefficient (molar-volume concentration basis); fugacity (atm); number of degrees of freedom
G	Gibbs energy (cal/mol)
$-\Delta G_{p,T}$	maximum useful work (cal/mol)
g	mass; statistical weight; weight; weight concentration
H	enthalpy (cal/mol)
Hal	halogen
h	heat of isothermal pressure increase; Planck constant
I	integration constant; ionic strength of solution; moment of inertia
i	conditional (empirical) chemical constant
j	quantum number of electronic energy levels; true chemical constant
K	equilibrium constant; partition coefficient
k	adiabatic exponent; Boltzmann constant; Henry's coefficient; number of components
L	relative enthalpy
l	distance; heat of isothermal expansion; length
M	molecular weight (mass)
Me	metal
m	mass; molality; number of bonds
N	normal concentration; number of components; number of molecules; total number of moles
N_A	Avogadro constant
n	number; valence
P	probability
p	pressure (atm)
Q	heat (cal/mol); partition function
q	number of relationships between concentrations of substances; quantity of electricity
R	molar gas constant *
r	radius; rotational quantum number
S	entropy (cal/mol·K)
s	number of different atoms; number of substances; spin quantum number
T	absolute temperature (K) **
t	temperature (°C)
U	internal energy (cal/mol)
V	hindering potential; volume (cm^3/mol)
v	velocity; vibrational quantum number

* The value of R in the book is taken equal to 1.987 cal/mol·K = 8.314×10^7 erg/mol·K = 0.848 kgf-m/mol·K = 82.06 cm^3·atm/mol·K.

** The value of $T_{0\,°C}$ in the numerical examples is taken equal to 273.2 K.

W	work done by a system (cal/mol)
W'	total work minus the work against the external pressure (cal/mol)
w	valence
x	mole fraction; unknown quantity
Y	partial molar quantity; thermodynamic parameter
y	activity coefficient; unknown quantity; yield of reaction (amount of reacted substance)
Z	atomic number; compression factor
z	charge of ion; number of gramme-equivalents; unknown quantity; valence of ion
α	angle; constant; cubic expansion coefficient; degree of dissociation; volume correction for real gas
β	constant; isothermal compressibility
γ	activity coefficient; isochoric pressure coefficient; ratio of heat capacities (C_p/C_V)
Δ	increment (a positive value corresponds to an increase in the relevant quantity)
δ	deviation; reduced volume
ε	energy
η	efficiency
Θ	characteristic temperature
θ	freezing point depression (K)
$\varkappa$	isothermal compressibility
λ	heat of isochoric pressure increase; wavelength
μ	chemical potential; deviation factor; Joule-Thomson coefficient
ν	constant; frequency; number of ions in dissociation of a molecule
$\tilde{\nu}$	wave number
ξ	extent of reaction
Π	osmotic pressure; thermodynamic potential
π	ratio of circumference to diameter of circle (3.14159); reduced pressure
ρ	density
Σ	function; sum
σ	surface tension; symmetry number
τ	reduced temperature
Φ	apparent molar quantity; correction factor
φ	function
χ	anharmonicity constant; heat of isobaric expansion
ω	compression factor for liquids

Superscripts (relating, as a rule, to a phase)

$^\circ$	pure substance or substance in the standard state

★	idealized state corresponding to an infinitely low pressure or infinite dilution
c	crystalline (solid) state
cd	condensed state (liquid or solid)
g	gaseous state
lq	liquid state

Subscripts

a	monoatomic
av	average
b	boiling
bas	basic
cal	calorimetric
comb	combustion
cond	condensation; conditional
cr	critical
diss	dissociation
e	electron(ic); eutectic
el	element
eq	equilibrium
exp	experimental
ext	external
f	fusion
form	formation
fr	free; freezing
h	hindered
i	ideal; internal
i	*i*-th component
in	initial; intramolecular
in.g	inert gas
irrev	irreversible
isot	isotope
m	melting
max	maximum
min	minimum
mix	mixture
n.b.p.	normal boiling point
nuc	nuclear
p	potential
ph.tr	phase transition
pr	product
r	reactant
rev	reversible
rot	rotational
s	surface
sp	spectroscopic

st	stable
subl	sublimation
theor	theoretical
tr	transformation; transition
trans	translational
unst	unstable
vap	vaporization
vib	vibrational
0	property of a system at $T = 0$ K
1	initial state; solvent
2	final state; solute

The Greek letter Δ in front of a thermodynamic function (for example ΔG) means that the change (final minus initial) is referred to.

The subscripts p, T, V and x indicate that the quantity they relate to is at constant pressure, temperature, volume or composition, respectively (for example C_p is the heat capacity at constant pressure).

A numerical subscript indicates the absolute temperature (decimal fractions are usually discarded) if it is not preceded by the symbol of another quantity.

APPENDIX 2

HEAT CAPACITIES, STANDARD ENTHALPIES AND GIBBS ENERGIES OF FORMATION, AND STANDARD ENTROPIES OF SELECTED SIMPLE SUBSTANCES, COMPOUNDS AND IONS *

Substance	Heat capacity: Coefficients of equation $C_p = \varphi(T)$			Heat capacity: Recommended temperature interval, K	Heat capacity: $(C_p^\circ)_{298}$, cal/mol·K	ΔH°_{298}, kcal/mol	ΔG°_{298}, kcal/mol	S°_{298}, e.u.
	a	$b \times 10^3$	$-c' \times 10^{-5}$					
I. Simple Substances								
Ag(c)	5.09	2.04	−0.36	273-1234	6.06	0	0	10.17
Al(c)	4.94	2.96	—	273-931.7	5.82	0	0	6.775
As(c)	5.23	2.22	—	298-1100	5.90	0	0	8.51
As_2(g)	8.93	—	0.52	298-2000	8.39	46.3	34.12	57.89
Au(c)	5.66	1.24	—	298-1336	6.07	0	0	11.33
B(c)	4.01	2.16	1.79	298-1700	2.65	0	0	1.40
Ba, α(c)	5.69	3.60	—	298-643	6.71	0	0	14.5
Be(c)	4.58	2.12	1.14	298-1556	3.93	0	0	2.28
Bi(c)	4.49	5.40	—	298-544.5	6.22	0	0	13.6
Br(g)	4.90	0.22	—	298-3500	4.968	26.73	19.69	41.803
Br_2(g)	8.92	0.12	0.30	331-3000	8.617	7.387	0.749	58.645
Br_2(lq)	18.09	—	—	298-331	18.09	0	0	36.38
C(c), diamond	2.27	3.06	1.54	298-1200	1.462	0.437	0.677	0.566
C(c), graphite	4.03	1.14	2.04	298-2500	2.04	0	0	1.372
Ca, α(c)	5.31	3.33	—	298-713	6.30	0	0	9.97
Cd, α (c)	5.31	2.94	—	298-594.1	6.22	0	0	12.37
Ce(c)	5.70	3.98	—	298-1027	6.44	0	0	15.3
Cl(g)	5.53	0.16	0.23	298-5000	5.22	28.993	25.174	39.455

Cl_2(g)	8.85	0.16	0.68	298-3000	8.112	0	0	53.293
Co, α(c)	4.74	4.00	—	298-700	5.93	0	0	7.18
Cr(c)	4.16	3.62	−0.30	298-2176	5.58	0	0	5.65
Cs(c)	1.96	18.2	—	273-301.5	7.50	0	0	20.16
Cu(c)	5.41	1.50	—	298-1357	5.84	0	0	7.923
D(g)	4.968	—	—	—	4.968	52.985	49.364	29.455
D_2(g)[a]	6.830	0.210	—	298-1500	6.978	0	0	34.622
F(g)	5.11	−0.04	−0.31	298-5000	5.436	19.00	14.92	37.92
F_2(g)	8.26	0.60	0.84	298-2500	7.49	0	0	48.45
Fe, α(c)	3.04	7.58	−0.60	298-1033	5.97	0	0	6.49
Ga(c)	5.70	0.25	0.13	100-302.9	6.23	0	0	9.82
Ge(c)	5.98	0.82	0.56	298-1210.4	5.59	0	0	7.44
H(g)	4.968	—	—	—	4.968	52.098	48.582	27.391
H_2(g)	6.52	0.78	−0.12	298-3000	6.891	0	0	31.195
HD(g)[b]	6.991	−0.274	—	298-1500	6.98	0.082	−0.346	34.345
Hf(c)	5.61	1.82	—	298-1400	6.15	0	0	10.41
Hg(lq)	6.44	—	−0.19	298-629.9	6.688	0	0	18.14
In(c)	4.59	6.04	—	298-429.3	6.39	0	0	13.82
Ir(c)	5.56	1.42	—	298-2727	6.00	0	0	8.48
I(g)	—	—	—	—	4.968	25.516	16.78	43.182
I_2(c)	9.59	11.90	—	298-386.8	13.01	0	0	27.76
I_2(g)	8.94	0.14	0.17	456-3000	8.817	14.922	4.629	62.284
K(c)	1.34	19.40	—	298-336.4	7.07	0	0	15.34
Li(c)	1.64	11.10	−0.84	298-453.7	5.91	0	0	6.75
Mg(c)	4.97	3.04	−0.04	298-922	5.95	0	0	7.81
Mn, α(c)	5.70	3.38	0.37	298-1000	6.28	0	0	7.65
Mo(c)	5.18	1.66	—	298-2890	5.75	0	0	6.85

[a] The table has been compiled mainly according to the data of [B50, 98; D2, 13, 14, 24, 113].

Appendix 2 (continued)

Substance	Heat capacity					ΔH°_{298}, kcal/mol	ΔG°_{298}, kcal/mol	S°_{298}, e.u.
	Coefficients of equation $C_p = \varphi(T)$			Recommended temperature interval, K	$(C_p^\circ)_{298}$, cal/mol·K			
	a	$b \times 10^3$	$-c' \times 10^{-5}$					
N(g)	4.968	—	—	—	4.968	112.981	108.888	36.613
N_2(g)	6.83	0.90	0.12	298-3000	6.961	0	0	45.769
Na(c)	4.02	9.04	—	298-371.0	6.75	0	0	12.24
Ni, α(c)	4.06	7.04	—	298-633	6.23	0	0	7.14
Ni, β(c)	6.00	1.80	—	633-1725	—	0	—	—
O_2(g)	7.16	1.00	0.40	298-3000	7.015	0	0	49.005
O_3(g)	9.86	2.46	−1.32	298-2000	9.38	34.0	38.90	57.08
Os(c)	5.69	0.88	—	298-3000	5.90	0	0	7.8
P(c), white	5.70	—	—	273-317	5.70	0	0	9.82
P(c), red	4.74	3.90	—	298-800	5.07	−4.15	−2.847	5.45
P(g)	4.968	—	—	—	4.968	75.637	66.944	38.788
P_2(g)	8.31	0.46	0.72	298-2000	7.66	34.38	24.705	52.09
P_4(g)	18.93	0.86	2.81	298-1500	16.05	14.104	5.872	66.89
Pb(c)	5.29	2.80	−0.23	298-600.6	6.32	0	0	15.49
Pd(c)	5.80	1.38	—	298-1828	6.18	0	0	9.00
Pt(c)	5.81	1.26	−0.06	298-2043	6.18	0	0	9.93
Rb(c)	3.27	13.1	—	273-312.6	7.38	0	0	18.22
S(c), monocl.	3.56	6.96	—	368.6-392	5.65	0.071	0.090	7.78
S(c), rhomb.	3.58	6.24	—	298-368.6	5.42	0	0	7.63
S(g)	5.26	−0.10	−0.36	298-2400	5.658	65.222	55.546	40.084
S_2(g)	8.72	0.16	0.90	298-3000	7.76	30.477	18.778	54.50

Sb(c)	5.51	1.74	—	273-903	6.03	0	0	10.92
Se(c)	3.30	8.80	—	298-491	6.06	0	0	10.07
Se(g)	5.13	0.36	0.22	298-2000	4.976	54.412	44.829	42.212
Se_2(g)	8.73	0.32	0.34	298-3000	8.46	33.136	21.186	60.22
Si(c)	5.70	0.70	1.04	298-1688	4.79	0	0	4.50
Sn(c), white	5.16	4.34	—	298-505	6.45	0	0	12.32
Sn(c), gray	—	—	—	—	6.16	−0.5	0.03	10.55
Sr, α(c)	5.71	2.66	—	298-862	6.3	0	0	12.5
Te(c)	4.57	5.28	—	298-723	6.16	0	0	11.83
Th, α(c)	5.17	4.56	—	298-1673	6.53	0	0	12.76
Ti, α(c)	5.25	2.52	—	298-1155	5.98	0	0	7.32
Tl, α(c)	5.26	3.46	—	298-507	6.29	0	0	15.34
U, α(c)	3.87	7.32	−0.49	298-941	6.61	0	0	12.02
V(c)	4.90	2.58	−0.20	298-2190	5.95	0	0	6.91
W(c)	5.74	0.76	—	298-3000	5.80	0	0	7.80
Zn(c)	5.35	2.40	—	298-692.7	6.08	0	0	9.95
Zr, α(c)	6.65	1.11	0.864	298-1136	6.06	0	0	9.32
II. Inorganic Compounds								
AgBr(c)	7.93	15.40	—	298-703	12.5	−24.06	−23.24	25.6
AgCl(c)	14.88	1.00	2.70	298-728	12.14	−30.73	−26.25	22.97
AgF(c)	—	—	—	—	11.5	−49.2	−44.91	20.0
AgI(c)	5.82	24.10	—	298-423	13.62	−14.80	−15.86	27.6
$AgNO_3$, α(c)	8.76	45.20	—	273-433	22.24	−29.76	−8.08	33.68
Ag_2CO_3(c)	19.57	24.36	—	298-500	26.88	−120.96	−104.5	40.0
Ag_2O(c)	11.13	15.48	—	298-500	15.74	−7 44	−2.69	28.91
Ag_2S, α(c)	10.13	26.40	—	298-452	18.29	−7.84	−9.76	34.42
Ag_2SO_4(c)	23.1	27.9	—	298-930	31.4	−171.42	−148.10	47.76
$AlCl_3$(c)	13.25	28.00	—	273-465.6	21.75	−168.3	−150.23	26.12
Al_2O_3, α(c), corundum	27.49	2.82	8.38	298-1800	18.89	−400.5	−378.17	12.17

Appendix 2 (continued)

Substance	Heat capacity					ΔH°_{298}, kcal/mol	ΔG°_{298}, kcal/mol	S°_{298}, e.u.
	Coefficients of equation $C_p = \varphi(T)$			Recommended temperature interval, K	$(C_p^\circ)_{298}$, cal/mol·K			
	a	$b \times 10^3$	$-c' \times 10^{-5}$					
$Al_2O_3 \cdot SiO_2$(c), kyanite	41.05	6.98	12.46	298-1500	29.10	−620.1	−584.16	20.02
$Al_2O_3 \cdot SiO_2$(c), sillimanite	39.30	8.04	11.02	298-1500	29.3	−618.8	−583.74	22.97
$Al_2O_3 \cdot SiO_2$(c), andalusite	41.22	6.24	12.22	298-1600	29.34	−619.6	−584.33	22.28
$3Al_2O_3 \cdot 2SiO_2$(c), mullite	111.29	13.06	33.22	298-2000	77.94	−1630.0	−1538.35	60.78
$Al_2(SO_4)_3$(c)	87.55	14.96	26.88	298-1100	62.0	−822.61	−741.13	57.17
$AsCl_3$(g)	19.72	0.10	1.46	298-2000	18.04	−64.8	−61.68	77.97
AsH_3(g)	10.07	5.42	2.20	298-2000	9.22	15.87	16.47	53.29
As_2O_3(c)	8.37	48.6	—	298-548	22.86	−159.2	−140.6	27.89
As_2O_5(c)	—	—	—	—	27.85	−221.42	−187.33	25.2
As_4O_6(c)	16.74	97.2	—	—	48.7	−319.0	−281.66	55.8
BCl_3(g)	18.45	0.80	3.28	298-2500	15.0	−96.51	−92.89	69.22
B_2O_3(c)	15.88	14.81	0.49	298-723	15.00	−304.23	−285.33	12.90
B_4C(c)	22.99	5.40	10.72	298-1700	12.62	—	—	6.48
$BaCl_2$(c)	17.00	3.34	—	298-1198	17.96	−205.0	−193.2	29.56
$BaCO_3$(c), witherite	21.50	11.06	3.91	298-1079	20.40	−297.5	−278.4	26.8
BaF_2(c)	13.98	10.20	—	298-1300	17.02	−286.9	−274.5	23.03
$Ba(NO_3)_2$(c)	30.05	35.70	4.01	298-850	36.18	−237.06	−190.0	51.1
BaO(c)	11.79	1.88	0.88	298-2000	10.82	−139.06	−132.0	16.8
$BaSO_4$(c)	33.80	—	8.43	298-1300	24.32	−350.2	−323.4	31.6
BeH_2(g)	—	—	—	—	6.985	76.77	69.51	42.24
BeO(c)	8.69	3.62	3.25	298-1000	6.10	−143.1	−136.12	3.38

$BiCl_3$(c)	−89.01	191.98	−53.33	298-503	26	−90.51	−74.84	41
Bi_2O_3(c)	24.74	8.00	—	298-800	27.13	−138.1	−118.87	36.2
Bi_2S_3(c)	28.90	6.10	—	298-1000	29.15	−37.2	−36.5	47.9
CCl_4(g)	24.17	1.20	4.10	298-1500	19.87	−24.6	−14.50	74.07
CN(g)	6.60	1.24	—	298-2000	6.97	102.28	95.09	48.41
C_2N_2(g)	14.90	3.20	2.04	298-2000	13.58	73.89	71.12	57.79
CO(g)	6.79	0.98	0.11	298-2500	6.958	−26.416	−32.778	47.214
CO_2(g)	10.57	2.10	2.06	298-2500	8.87	−94.052	−94.259	51.07
$COCl_2$(g)	16.051	2.894	2.159	298-1000	13.79	−52.80	−49.41	67.81
COS(g)	11.33	2.18	1.83	298-1800	9.92	−33.9	−40.40	55.32
CS_2(g)	12.45	1.60	1.80	298-1800	10.37	27.74	15.75	56.83
CaC_2, α(c)	16.40	2.84	2.07	298-720	14.94	−14.1	−15.32*	16.8
CaC_2, β(c)	15.40	2.00	—	720-1500	—	—	—	—
$CaCO_3$(c), calcite	24.98	5.24	6.20	298-1200	19.57	−288.45	−269.78	22.2
$CaCl_2$(c)	17.18	3.04	0.60	298-1055	17.35	−191.1	−173.91*	27.2
CaF_2, α(c)	14.30	7.28	−0.47	298-1424	16.02	−290.3	−277.7	16.46
CaH_2(c)	—	—	—	—	—	−44.5	−32.6*	~10
CaO(c)	11.67	1.08	−1.56	298-1800	10.24	−151.79	−144.3	9.50
$CaO \cdot Al_2O_3$(c)	36.00	5.96	7.96	298-1800	28.83	556.0	−527.9	27.3
$CaO \cdot Al_2O_3 \cdot 2SiO_2$, α(c), anorthite	64.42	13.70	16.89	298-1700	50.46	−1009.54	−955.9	48.4
$3CaO \cdot Al_2O_3$(c)	62.28	4.58	12.01	298-1800	50.14	−857.45	−815.35	49.1
$2CaO \cdot Al_2O_3 \cdot SiO_2$(c), gehlenite	63.74	8.00	15.12	298-1700	49.10	−952.9	−904.6	47.4
$CaO \cdot B_2O_3$(c)	31.02	9.76	8.07	298-1435	24.85	−485.41	−459.90	25.1
$2CaO \cdot B_2O_2$(c)	43.75	11.50	10.69	298-804	35.16	−653.54	−620.59	34.7
$3CaO \cdot SiO_2$(c)	49.85	8.62	10.15	298-1800	41.08	−700.09	−665.15	40.3
$Ca(OH)_2$(c)	19.07	10.80	—	298-700	20.91	−235.71	−214.77	19.93
$CaMg(SiO_3)_2$(c), diopside	52.87	7.84	15.74	298-1600	39.80	−766.2	−724.5	34.2

* Calculated by the author.

Appendix 2 (continued)

Substance	Heat capacity					ΔH°_{298}, kcal/mol	ΔG°_{298}, kcal/mol	S°_{298}, e.u.
	Coefficients of equation $C_p = \varphi(T)$			Recommended temperature interval, K	$(C_p^\circ)_{298}$, cal/mol·K			
	a	$b \times 10^3$	$-c' \times 10^{-5}$					
$Ca(NO_3)_2$(c)	29.37	36.80	4.13	298-800	35.70	−224.00	−177.34	46.2
CaS(c)	10.20	3.80	—	298-1000	11.33	−115.3	−114.1	13.5
$CaSO_4$(c), anhydride	16.78	23.60	—	298-1468	23.82	−342.42	−315.56	25.5
$CaSO_4 \cdot 2H_2O$(c), gypsum	21.84	76.00	—	298-400	44.5	−483.06	−429.19	46.36
$CaSiO_3$(c), wollastonite	26.64	3.60	6.52	298-1450	20.38	−390.76	−370.30	19.6
Ca_2SiO_4, β(c)	34.87	9.74	6.26	298-970	30.74	−551.49	−524.00	30.5
$Ca_3(PO_4)_2$, α(c)	48.24	39.68	5.00	298-1373	55.35	−986.2	−929.7	57.6
$CdBr_2$(c)	—	—	—	—	18.32	−75.35	−70.71	33.18
$CdCO_3$(c)	—	—	—	—	—	−180.36	−166.2	23
$CdCl_2$(c)	14.64	9.60	—	273-841	17.84	−93.40	−82.04	27.55
CdO(c)	9.78	2.02	—	298-2086	10.43	−61.9	−54.81	13.1
$Cd(OH)_2$(c)	—	—	—	—	—	−134.2	−113.23	22.24
CdS(c)	12.90	0.90	—	298-1273	11.31	−37.5	−36.61	17.0
$CdSO_4$(c)	18.48	18.5	—	298-1273	23.81	−223.33	−196.91	29.41
ClO_2(g)	11.54	1.80	1.85	298-1500	10.03	25	29.24	61.43
Cl_2O(g)	12.71	0.80	1.86	298-2000	10.85	18.3	22.52	63.63
$CoCl_2$(c)	14.41	14.60	—	298-1000	18.76	−74.1	−63.88	26.21
CoS(c)	10.60	2.51	—	298-1373	11.3	−19.8	−20.2	14.9
$CoSO_4$(c)	30.10	9.92	—	298-1200	24.67	−212.46	−187.19	28.07
$CrCl_2$(c)	17.20	3.90	1.20	298-1000	17.01	−94.56	−85.15	26.09
Cr_2O_3(c)	28.53	2.20	3.736	298-1800	28.38	−272.7	−253.2	19.4

CsCl(c)	12.18	12.28	4.56	298-740.5	12.54	−103.97	−97.23	24.18
CuBr(c)	12.80	1.58	—	298-761	13.08	−24.74	−23.80	22.97
CuCl(c)	5.88	19.20	—	298-703	11.6	−32.81	−28.70	20.8
$CuCl_2$(c)	15.42	12.00	—	298-800	17.18	−51.52	−40.07	25.83
CuI(c)	12.10	2.86	—	298-675	12.9	−16.26	−16.65	23.1
CuO(c)	11.53	1.88	1.76	298-1400	10.11	−38.72	−30.92	10.19
CuS(c), covellite	10.60	2.64	—	298-1273	11.43	−12.7	−12.80	15.9
$CuSO_4$(c)	18.77	17.20	—	273-900	23.63	−184.25	−158.17	26.1
$CuSO_4 \cdot 5H_2O$(c)	—	—	—	—	67.2	−544.78	−449.30	71.8
Cu_2O(c)	14.08	5.88	0.76	298-1515	15.21	−41.39	−35.98	22.21
Cu_2S, α(c)	9.38	31.2	—	273-376	18.24	−19.0	−20.6	28.9
D_2O(g)	7.69	2.96	0.34	298-2200	8.207	−59.561	−56.060	47.381
D_2O(lq)	—	—	—	—	20.15	−70.411	−58.192	18.14
F_2O(g)	12.48	0.98	2.16	298-1500	10.35	6.0	10.15	59.03
$FeCO_3$(c), siderite	11.63	26.8	—	298-885	19.63	−180.0	−162.6	22.97
$FeCl_2$(c)	18.94	2.08	1.17	298-950	18.25	−81.68	−72.26	28.2
$Fe_{0.95}O$(c), wüstite	11.66	2.00	0.67	298-1650	11.50	−63.64	−58.59	13.74
$Fe(OH)_2$(c)	—	—	—	—	23.2	−135.8	−115.57	21
FeS, α(c)	5.19	26.40	—	298-411	12.08	−24.0	−24.09	14.41
FeS, β(c)	10.95	3.80	—	411-1468	13.0	−21.35	−21.0*	—
FeS_2(c), pyrite	17.88	1.32	3.05	298-1000	14.86	−39.0	−36.29	12.65
$FeSO_4$(c)	—	—	—	—	24.04	−221.7	−195.93	25.7
FeSi(c)	10.72	4.30	—	298-900	11.6	−18.3	−18.3	11.0
$FeTiO_3$(c), ilmenite	27.87	4.36	4.79	298-1640	23.78	−299.55	−277.05	25.3
Fe_2O_3(c), hematite	23.49	18.60	3.55	298-950	24.8	−196.5	−176.95	20.9
Fe_2SiO_4(c)	36.51	9.36	6.70	298-1490	31.76	−353.2	−329.11	34.7
Fe_3C, α(c)	19.64	20.00	—	298-463	25.3	6.0	4.49	25.9

* Calculated by the author.

Appendix 2 (continued)

Substance	Heat capacity					ΔH°_{298}, kcal/mol	ΔG°_{298}, kcal/mol	S°_{298}, e.u.
	Coefficients of equation $C_p = \varphi(T)$			Recommended temperature interval, K	$(C^\circ_p)_{298}$, cal/mol·K			
	a	$b \times 10^3$	$-c' \times 10^{-5}$					
Fe_3C, β(c)	25.62	3.00	—	463-1500	—	5.5	4.5*	—
Fe_3O_4(c), magnetite	39.92	18.86	10.01	298-1100	36.04	−267.0	−242.39	34.94
HBr(g)	6.41	1.24	−0.15	298-2000	6.965	−8.67	−12.75	47.464
HCN(g)	8.92	3.10	1.12	298-2000	8.57	32.2	29.7	48.21
HCl(g)	6.27	1.24	−0.30	298-2000	6.963	−22.06	−22.78	44.644
HF(g)	6.55	0.72	−0.17	298-4000	6.964	−64.7	−65.2	41.51
HI(g)	6.39	1.42	−0.14	298-2000	6.967	6.35	0.425	49.35
HNO_3(lq)	—	—	—	—	26.26	−41.62	−19.322	37.20
H_2O(g)	7.30	2.46	—	298-2750	8.025	−57.796	−54.638	45.106
H_2O(lq)	12.65	11.38	1.73	273-373	17.997	−68.315	−56.703	16.75
H_2O_2(lq)	12.81	28.00	—	298-450	21.35	−44.88	−28.77	26.17
H_2S(g)	7.81	2.96	0.46	298-2300	8.18	−5.0	−8.081	49.16
H_2SO_4(lq)	—	—	—	—	33.20	−194.6	−164.98	37.50
H_2Se(g)	7.59	3.50	0.31	298-2000	8.28	8	4.71	52.3
H_2Te(g)	8.48	2.88	0.74	298-2000	8.50	23.83	20.36	54.69
$HgBr_2$(c)	—	—	—	—	18.2	−40.6	−37.16	42.98
$HgCl_2$(c)	11.73	16.36	—	298-428	17.7	−54.55	−43.23	33.47
HgI_2(c), red	17.41	4.00	—	273-403	18.7	−25.2	−24.63	43.99
HgO(c), red	8.33	7.37	—	298-769	10.53	−21.72	−14.02	16.80
HgS, α(c), red	10.90	3.65	—	298-853	11.57	−14.1	−12.3	19.7
Hg_2Br_2(c)	—	—	—	—	—	−49.49	−43.34	52.03

Hg_2CO_3(c)	—	—	—	—	24.7*	−132.24	−112.0	43.27
Hg_2Cl_2(c)	22.10	7.40	—	273-798	23.88	−63.35	−50.38	46.07
Hg_2I_2(c)	22.80	9.22	—	298-563	23.4	−28.9	−26.57	56.23
Hg_2SO_4(c)	—	—	—	—	31.54	−177.98	−149.97	47.97
$KAl(SO_4)_2$(c)	55.96	19.68	13.96	298-1100	46.12	−589.24	−534.29	48.9
$KAlSi_3O_8$(c), microcline	63.83	12.90	17.05	298-1400	—	−946.27	−892.83	52.5
KBr(c)	10.65	4.52	−0.49	298-1000	12.46	−94.10	−90.20	22.93
KCl, α(c)	9.89	5.20	−0.77	298-1043	12.26	−104.37	−97.70	19.73
$KCl \cdot MgCl_2$(c)	25.92	17.60	—	298-760	31.2**	−260.7	243.7*	—
$KClO_3$(c)	—	—	—	—	23.96	−93.50	−69.29	34.17
KF, α(c)	11.27	3.86	0.69	298-500	11.79	−135.6	−128.52	15.92
KI(c)	11.36	4.00	—	298-950	13.16	−78.95	−77.66	24.9
$KMnO_4$(c)	—	—	—	—	28.10	−198.11	−174.27	41.0
KNO_3(c)	14.55	28.40	—	298-401	23.01	−117.76	−93.96	31.81
$K_2Cr_2O_7$(c)	36.66	54.80	—	298-671	52.50	−494.09	−451.17	69.6
K_2SO_4, α(c)	28.77	23.80	4.26	298-856	31.42	−342.66	−314.62	41.96
LiCl(c)	10.20	5.21	0.22	298-883	11.48	−97.58	−91.79	14.17
$LiNO_3$(c)	14.98	21.20	—	298-525	19.9	−115.28	−91.7*	17*
Li_2CO_3(c)	—	—	—	—	23.00	−290.64	−270.60	21.55
Li_2SO_4(c)	28.43	22.31	6.50	298-505	28.10	−343.18	−315.67	27.24
$MgCO_3$(c), magnesite	18.62	13.80	4.16	298-750	18.07	−266.0	−246.02	15.70
$MgCl_2$(c)	18.90	1.42	2.06	298-987	17.06	−153.35	−141.52	21.42
MgF_2(c)	16.93	2.52	2.20	298-1536	14.72	−268.7	−256.0	13.68
$Mg(NO_3)_2$(c)	10.68	71.20	−1.79	298-600	33.92	−188.72	−140.63	39.2
MgO(c)	10.18	1.74	1.48	298-2100	8.88	−143.70	−135.98	6.44
$Mg(OH)_2$(c)	13.04	15.80	—	298-600	18.41	−221.0	−199.25	15.10
$MgSO_4$(c)	—	—	—	—	23.02	−301.57	−274.26	21.84

* Calculated by the author.
** Calculated on the basis of the coefficients given in the table.

Appendix 2 (continued)

Substance	Heat capacity					ΔH°_{298}, kcal/mol	ΔG°_{298}, kcal/mol	S°_{298}, e.u.
	Coefficients of equation $C_p = \varphi(T)$			Recommended temperature interval, K	$(C_p^\circ)_{298}$, cal/mol·K			
	a	$b \times 10^3$	$-c' \times 10^{-5}$					
$MgSiO_3$(c), clinoenstatite	24.55	4.74	6.28	298-1600	19.55	−370.11	−349.33	16.19
$MgTiO_3$(c)	28.29	3.28	6.53	298-1800	21.92	−375.50	−354.37	17.80
Mg_2SiO_4(c)	35.81	6.54	8.52	298-1800	28.24	−520.24	−491.72	22.73
$MnCO_3$(c), rhodochrosite	21.99	9.30	4.69	298-700	19.48	−213.9	−197.3*	26.98
$MnCl_2$(c)	18.04	3.16	1.37	298-923	17.43	−115.2	−105.4	28.26
MnO(c)	11.11	1.94	0.88	298-1800	10.54	−92.0	−86.75	14.27
MnO_2(c)	16.60	2.44	3.88	298-800	12.91	−124.4	−111.3	12.68
MnS(c)	11.40	1.80	—	298-1803	11.94	−51.01	−52.0	18.7
$MnSO_4$(c)	29.26	8.92	7.04	298-1100	24.02	−269.6	−238.9	26.8
$MnSiO_3$(c)	26.42	3.88	6.16	298-1500	20.66	−315.64	−296.55	21.3
Mn_3C(c)	25.26	5.60	4.07	298-1310	22.33	−3.6	−3.75	23.6
NH_3(g)	7.11	6.00	0.37	298-1800	8.50	−11.04	−3.993	46.04
$NH_4Al(SO_4)_2$(c)	79.77	—	22.80	298-700	54.1	−562.5	−487.48	51.7
NH_4Cl(c)	11.80	32.00	—	298-457.7	20.1	−75.10	−48.558	22.9
NH_4HCO_3(c)	—	—	—	—	—	−203.2	(−160.3)	28.3
NH_4HSO_4(c)	10.00	81.00	—	298-417	32.4	−245.10	—	15.0
$NH_4H_2PO_4$(c)	—	—	—	—	34.0	−345.5	−289.40	36.32
NH_4NO_3(c), rhomb.	—	—	—	—	33.3	−87.34	−43.94	36.1
$(NH_4)_2SO_4$(c)	24.77	67.20	—	298-600	44.8	−282.09	−215.43	52.6
NO(g)	7.03	0.92	0.14	298-2000	7.14	21.57	20.693	50.33
NO_2(g)	10.26	2.04	1.61	298-2000	8.96	8.0	12.32	57.40

NOCl(g)	10.73	1.84	1.66	298-2000	10.68	12.54	15.97	62.53
N_2O(g)	10.92	2.06	2.04	298-2000	9.23	19.6	24.884	52.55
N_2O_4(g)	20.05	9.50	3.56	298-1000	18.8	2.3	23.522	72.6
N_2O_5(g)	—	—	—	—	22.7	2.8	27.63	85.0
$NaAlSi_3O_8$(c), albite	61.70	13.90	15.01	298-1400	48.97	−937.15	−883.98	50.2
NaBr(c)	11.87	2.10	—	298-550	12.28	−86.38	−83.5*	21.8*
NaCl(c)	10.98	3.90	—	298-1073	12.07	−98.26	−91.79	17.24
$NaClO_3$(c)	13.07	37.00	—	298-528	25.0*	−80.78	−63.21	53.4
NaF(c)	10.40	3.88	0.33	298-1285	11.20	−137.1	−129.87	12.26
$NaHCO_3$(c)	10.19	36.06	—	298-400	20.94	−226.5	−203.6	24.4
NaI(c)	12.5	1.62	—	298-936	12.45	−69.46	−68.2*	24.0*
$NaNO_3$(c)	6.34	53.32	—	298-549.2	22.24	−111.54	−87.45	27.85
NaOH, α(c)	0.24	32.42	−3.87	298-566	14.23	−101.9	−90.87	15.40
Na_2CO_3(c)	27.13	15.62	4.78	298-1124	26.53	−270.26	−250.50	33.17
Na_2O(c)	15.70	5.40	—	298-1100	17.44	−99.40	−90.13	17.99
Na_2SO_4, α(c)	14.97	52.90	—	298-514	30.50	−330.90	−302.78	35.73
$Na_2SO_4 \cdot 10H_2O$(c)	—	—	—	—	140.4	−1033.48	−870.93	140.5
Na_2SiO_3(c)	31.14	9.60	6.47	298-1361	26.90	−372.32	−349.78	27.21
$Na_2Si_2O_5$(c)	44.38	16.86	10.67	298-1147	37.50	−590.1	−555.3	39.37
Na_2TiO_3, α(c)	25.18	20.72	—	298-560	30.02	−379.5	−356.8	29.1
Na_3AlF_6(c)	45.95	29.46	2.78	298-845	51.6	−790.0	−750.64	57.00
Na_4SiO_4(c)	—	—	—	—	43.79	−497.8	−466.6	46.8
$NiCO_3$(c)	—	—	—	—	20.6	−166	−147.69	20.6
$NiCl_2$(c)	17.5	3.16	1.19	298-1303	17.13	−72.7	−61.67	23.44
NiO, α(c)	−4.99	37.58	−3.89	298-525	10.59	−57.30	−50.57	9.08
$Ni(OH)_2$(c)	—	—	—	—	—	−129.90	−109.55	19.1
NiS(c)	9.25	6.40	—	298-597	11.26	−19	−18.37	12.66

* Calculated by the author.

Appendix 2 (continued)

Substance	Heat capacity					ΔH°_{298}, kcal/mol	ΔG°_{298}, kcal/mol	S°_{298}, e.u.
	Coefficients of equation $C_p = \varphi(T)$			Recommended temperature interval, K	$(C_p^\circ)_{298}$, cal/mol·K			
	a	$b \times 10^3$	$-c' \times 10^{-5}$					
$NiSO_4$(c)	30.10	9.92	—	298-1200	23.35	−208.77	−18.55	24.82
OH(g)	6.45	0.88	−0.38	298-3000	7.143	9.31	8.18	43.890
PBr_3(g)	18.154	2.045	0.153	298-800	18.2	−31.6	−37.21	83.2
PCl_3(g)	20.068	0.289	2.706	298-1000	17.17	−66.8	−62.25	74.50
PCl_5(g)[c]	4.739	107.328	—	298-500	27.0	−87.7	−71.02	87.1
PF_3(g)	17.18	1.92	3.88	298-2000	14.03	−228.8	−223.63	65.15
PH_3(g)	9.11	5.72	1.71	298-2000	8.87	1.3	3.2	50.24
$POCl_3$(g)	22.12	3.60	2.69	298-1000	20.2	−133.58	−122.59	77.4
P_4O_{10}(c)	16.75	108.0	—	298-631	50.6	−713.2	−644.7	54.7
$PbBr_2$(c)	18.59	2.20	—	298-761	19.25	−67.5	−63.54	38.66
$PbCO_3$(c), cerussite	12.39	28.6	—	298-800	20.9	−167.2	−149.59	31.3
$PbCl_2$(c)	15.96	8.00	—	298-771	18.4	−86.00	−75.06	32.09
PbF_2(c)	12.58	17.17	—	298-720	17.7	−161.7	−150.69	27.0
PbI_2(c)	18.00	4.70	—	298-685	19.4**	−41.88	−41.18	41.91
PbO(c), yellow	11.08	2.71	0.85	762-1170	10.94	−52.01	−44.98	16.42
PbO(c), red	8.64	7.76	—	298-762	10.95	−52.41	−45.20	15.8
$Pb(OH)_2$(c)	—	—	—	—	—	−122.5	−107.85	21
PbO_2(c)	12.7	7.80	—	298-1000	15.48	−66.10	−52.18	17.19
PbS(c)	10.66	3.92	—	298-900	11.90	−24.0	−23.61	21.8
$PbSO_4$(c)	10.96	31.00	−4.20	298-1100	24.67	−220.04	−194.51	35.51

Pb_3O_4(c)	—	—	—	—	35.1	−172.9	−144.88	50.5
$Pb_3(PO_4)_2$(c)	—	—	—	—	61.2	−620.3	−581.4	84.4
SF_6(g)	31.89	4.20	9.01	298-2000	23.3	−288.5	−263.67	69.7
SO(g)	8.26	0.32	1.00	298-3000	7.21	0.1	−6.128	53.02
SO_2(g)	11.04	1.88	1.84	298-2000	9.53	−70.96	−71.752	59.29
SO_2Cl_2(g)	21.10	3.86	3.40	298-1000	18.5	−86.6	−76.207	74.4
SO_3(g)	13.90	6.10	3.22	298-1500	12.11	−94.61	−88.71	61.35
$SbCl_3$(c)	10.3	51.1	—	298-346	26.4	−91.1	−77.07	43.8
Sb_2O_5(c)	—	—	—	—	28.11	−240.8	−206.68	29.9
Sb_4O_6(c)	38.2	34.2	—	298-929	53.5	−338.7	−298.96	67.4
Sb_2S_3(c), black	24.2	13.2	—	298-821	29.45	−37.7	−37.30	43.4
SeF_6(g)	34.86	1.96	8.13	298-2000	26.4	−246	−222.02	75.0
$SiBr_4$(g)	25.19	0.64	1.94	298-1000	23.2	−100.3	−104.16	90.2
SiC(c), hexagon.	9.93	1.92	3.66	298-2000	6.38	−15.0	−14.48	39.4
$SiCl_4$(g)	24.25	1.64	2.75	298-2000	21.6	−157.15	−147.61	79.1
SiF_4(g)	21.95	2.66	4.72	298-2000	17.6	−385.98	−375.84	67.4
SiH_4(g)	11.05	8.78	3.05	298-1800	10.25	8.31	13.67	48.89
SiO_2(c), α-quartz	11.22	8.20	2.70	298-848	10.62	−217.72	−204.75	10.00
SiO_2(c), β-quartz	14.41	1.94	—	848-2000	—	—	—	—
SiO_2(c), α-cristobalite	4.28	21.06	—	298-523	10.56	−217.08	−204.17	10.2
SiO_2(c), β-cristobalite	14.40	2.04	—	523-2000	10.66	−216.4	−203.55	10.4
SiO_2(c), α-tridymite	3.27	24.80	—	298-390	10.66	−217.27	−204.42	10.4
SiO_2(c), β-tridymite	13.64	2.64	—	390-1953	10.66	−204.8	−191.9	11.2
SiO_2, glass	13.38	3.68	3.45	298-2000	10.60	−215.94	−203.33	11.2
Si_3N_4(c)	16.83	23.6	—	298-900	23.87	−177.7	−153.6	24.2
$SnCl_2$(c)	16.2	9.26	—	273-520	19.0**	−79.1	−73.9*	—
$SnCl_4$(lq)	—	—	—	—	39.5	−126.4	−109.4	61.9

* Calculated by the author.
** Calculated on the basis of the coefficients given in the table.

Appendix 2 (continued)

Substance	Heat capacity					ΔH°_{298}, kcal/mol	ΔG°_{298}, kcal/mol	S°_{298}, e.u.
	Coefficients of equation $Cp = \varphi(T)$			Recommended temperature interval, K	$(C_p^\circ)_{298}$, cal/mol·K			
	a	$b \times 10^3$	$-c' \times 10^{-5}$ $(c \times 10^6)$*					
$SnO(c)$	9.95	3.50	—	298-1273	10.6	−68.35	−61.40	13.5
$SnO_2(c)$	17.66	2.40	5.16	298-1500	12.6	−138.81	−124.25	12.5
$Sn(OH)_2(c)$	—	—	—	—	—	−116.93	−117.6	23.1
SnS, α(c)	8.53	7.48	−0.90	298-875	11.77	−26.33	−25.87	18.4
$SrCO_3(c)$	23.52	6.32	5.08	298-1197	19.46	−294.6	−275.5	23.2
$SrCl_2(c)$	15.28	8.09	—	298-940	18.9	−198.2	−187.5	30.0
SrO(c)	12.34	1.12	1.806	298-1200	10.64	−144.44	−137.3	13.00
$SrSO_4(c)$	21.80	13.30	—	298-1500	24.8	−350.82	−323.46	26.5
$ThCl_4(c)$	—	—	—	—	—	−285.4	−264.0	46.8**
$ThO_2(c)$	15.84	2.88	1.60	298-2000	15.59	−293.2	−279.4	14.76
TiC(c)	11.83	0.80	3.58	298-2000	8.11	−44.5	−43.37	5.80
$TiCl_4(g)$	25.45	0.24	2.36	298-2000	22.88	—	—	84.4
TiO, α(c)	10.57	3.60	1.86	298-1264	9.56	−123.90	−116.89	8.33
$TiO_2(c)$, rutile	17.97	0.28	4.35	298-1800	13.20	−225.5	−212.28	12.01
TlCl(c)	10.80	4.60	—	298-704	12.17	−48.79	−44.20	26.59
TlBr(c)	9.95	7.10	—	298-733.2	12.55	−41.2	−39.7	28.5
$UO_2(c)$	19.20	1.62	3.96	298-2000	15.33	−259.5	−246.9	18.63
$VCl_3(c)$	22.99	3.92	1.68	298-900	22.27	−140.0	−123.45	31.3
$V_2O_3(c)$	29.35	4.76	5.42	298-1800	24.67	−291.29	−272.22	23.58
WO_3, α(c)	21.26	3.38	4.42	298-1050	17.60	−201.46	−182.62	18.14
$ZnCO_3(c)$, smithsonite	9.30	33.00	—	298-780	19.14	−195.52	−176.1	19.7
$ZnCl_2(c)$	14.50	5.50	—	298-588.6	17.03	−99.20	−88.29	26.64

ZnO(c)	11.71	1.22	2.18	298-2000	9.62	−83.80	−76.64	10.43
ZnS(c), sphalerite	11.77	1.26	1.16	298-1300	10.88	−49.1	−47.97	13.80
$ZnSO_4$(c)	17.07	20.80	—	298-1000	23.68	−234.55	−207.96	26.42
$ZrCl_4$(c)	31.92	—	2.91	298-700	28.65	−234.7	−212.48	41.35

Note: The coefficient $c \times 10^5$ of the equation $Cp = \varphi(T)$ equals: [a] 0.468; [b] 0.598; [c] −119.20.

III. Organic Compounds

Hydrocarbons

CH_4(g), methane	3.422	17.845	−4.165	291-1500	8.51	−17.88	−12.146	44.53
C_2H_2(g), acetylene[a]	12.13	3.84	—	298-2000	10.53	54.02	49.827	48.00
C_2H_4(g), ethene	2.706	29.160	−9.059	291-1500	10.26	12.54	16.334	52.41
C_2H_6(g), ethane	1.375	41.852	−13.827	291-1000	12.59	−20.25	−7.883	54.85
C_3H_4(g), methylacetylene	4.41	37.61	14.38	—	14.50	44.32	46.47	59.30
C_3H_4(g), propadiene	3.62	36.17	−12.16	—	14.10	45.92	48.37	58.30
C_3H_6(g), propene	2.974	45.024	−11.376	270-510	15.27	4.88	14.99	63.80
C_3H_6(g), cyclopropane	—	—	—	—	13.37	12.74	24.95	56.75
C_3H_8(g), propane	0.410	64.71	−22.582	298-1500	17.57	−24.82	−5.61	64.51
C_4H_6(g), butadiene-1,3	2.31	58.28	20.95	—	19.01	26.33	36.01	66.62
C_4H_6(g), dimethylacetylene	—	—	—	—	18.63	34.97	44.32	67.71
C_4H_8(g), butene-1	5.132	61.760	−19.322	298-1500	20.47	−0.03	17.04	73.04
C_4H_8(g), *cis*-butene-2	2.047	64.311	−19.834	298-1500	18.86	−1.67	15.74	71.90
C_4H_8(g), *trans*-butene-2	4.967	59.961	−18.147	298-1500	20.99	−2.67	15.05	70.86
C_4H_8(g), 2-methylpropene	5.331	60.246	−18.140	298-1500	21.30	−4.04	13.88	70.17
C_4H_{10}(g), butane	4.357	72.552	−22.145	298-1500	23.29	−30.15	−4.10	74.12
C_4H_{10}(g), isobutane	2.296	82.407	−38.792	298-1500	23.14	−32.15	−4.99	70.42
C_5H_{12}(g), 2-methylbutane	−0.283	47.936	−26.26	298-1500	28.39	−36.92	−3.54	82.12
C_5H_{12}(g), 2,2-dimethylpropane	6.076	98.954	−35.369	298-1500	29.07	−39.67	−3.64	73.23
C_5H_{12}(g), pentane	3.140	100.532	−35.560	298-1500	28.73	−35.00	−2.00	83.40

* For organic compounds.
** Calculated by the author.

Appendix 2 (continued)

Substance	Heat capacity					ΔH°_{298}, kcal/mol	ΔG°_{298}, kcal/mol	S°_{298}, e.u.
	Coefficients of equation $C_p = \varphi(T)$			Recommended temperature interval, K	$(C_p^\circ)_{298}$, cal/mol·K			
	a	$b \times 10^3$	$-c \times 10^6$					
C_6H_6(g), benzene	−5.04	95.63	−40.6	—	19.52	19.82	30.99	64.34
C_6H_6(lq), benzene	—	—	—	—	32.3	11.72	29.72	41.41
C_6H_{12}(g), cyclohexane	−7.701	125.675	−41.584	298-1500	25.40	−29.43	7.59	71.28
C_6H_{12}(lq), cyclohexane	—	—	—	—	37.4	−37.34	6.37	48.84
C_6H_{14}(g), hexane	7.313	104.906	−32.397	298-1500	34.20	−39.96	−0.06	92.83
C_7H_8(g), toluene	4.74	113.46	−46.7	—	24.77	11.95	29.16	76.64
C_7H_8(lq), toluene	—	—	—	—	37.3	2.87	27.19	52.81
C_7H_{16}(g), heptane	5.401	136.29	−48.771	298-1500	39.67	−44.88	1.91	102.27
C_8H_8(g), styrene	—	—	—	—	44.56	−2.98	28.61	60.99
C_8H_{10}(g), ethylbenzene	−3.13	130.4	−52.9	—	30.69	7.12	31.21	86.15
C_8H_{10}(g), *o*-xylene	4.603	104.476	−33.616	298-1500	29.18	35.22	51.10	82.48
C_8H_{10}(lq), *o*-xylene	—	—	—	—	44.9	−5.84	26.40	58.8
C_8H_{10}(g), *m*-xylene	1.956	109.147	−35.583	298-1500	30.49	4.12	28.41	85.49
C_8H_{10}(lq), *m*-xylene	—	—	—	—	43.8	−6.07	25.73	60.27
C_8H_{10}(g), *p*-xylene	1.846	108.594	−35.200	298-1500	30.32	4.29	28.95	84.23
C_8H_{10}(lq), *p*-xylene	—	—	—	—	43.9	−5.84	26.28	59.20
C_8H_{18}(g), octane	0.231	155.942	−55.857	298-1500	45.14	−49.82	3.92	111.55
$C_{10}H_8$(c), naphthalene	—	—	—		39.5	18.66	48.05	39.89
$C_{12}H_{10}$(c), biphenyl	—	—	—	—	47.1	24.02	60.75	49.2
$C_{14}H_{10}$(c), anthracene	—	—	—	—	49.7	30.87	68.3	49.58
$C_{14}H_{10}$(c), phenanthrene	—	—	—	—	56.0	27.76	64.87	50.63

				Alcohols, Ethers, Aldehydes, Ketones, Acids				
CH_4O(g), methanol	4.88	24.78	−5.889	300-700	10.49	−48.27	−39.04	57.29
CH_4O(lq), methanol	—	—	—	—	19.15	−57.23	−39.94	30.26
C_2H_6O(g), ethanol	3.578	49.847	16.991	300-1000	15.64	−56.07	−40.17	67.54
C_2H_6O(lq), ethanol	—	—	—	—	26.76	−66.19	−41.64	38.48
C_3H_8O(g), propanol	−0.62	74.67	25.22	—	20.82	−61.55	−38.95	77.63
C_3H_8O(g), *iso*-propanol	—	—	—	—	21.21	−65.15	−41.49	74.07
C_3H_8O(lq), *iso*-propanol	—	—	—	—	39.0	−76.4	−44	43.0
$C_4H_{10}O$(g), diethyl ether	—	—	—	—	26.89	−60.28	−29.24	81.90
$C_4H_{10}O$(lq), diethyl ether	—	—	—	—	40.2	−66.8	−29.38	60.5
CH_2O(g), formaldehyde	4.498	13.953	−3.730	291-1500	8.46	−27.7	−26.27	52.26
C_2H_4O(g), acetaldehyde	7.422	29.029	−8.742	298-1500	13.22	−39.8	−31.86	63.01
C_7H_6O(lq), benzaldehyde	—	—	—	—	40.5	−21.3	—	49.4
C_3H_6O(g), acetone	5.371	48.227	−15.182	298-1500	17.90	−52.00	−36.58	70.49
CH_2O_2(g), formic acid	7.33	21.32	−8.255	300-700	10.81	−90.58	−83.98	59.45
CH_2O_2(lq), formic acid	—	—	—	—	23.67	−101.7	−86.57	30.82
$C_2H_4O_2$(g), acetic acid	5.20	46.16	−18.35	300-700	15.9	−103.2	−89.29	67.5
$C_2H_4O_2$(lq), acetic acid	—	—	—	—	29.5	−115.7	−93.06	38.2
$C_2H_2O_4$(c), oxalic acid	—	—	—	—	25.3	−196.3	−165.52	28.7
$C_7H_6O_2$(c), benzoic acid	—	—	—	—	34.7	−92.05	−58.62	40.05
				Halogen and Nitrogen Derivatives, Phenol				
$CHBr_3$(g)[b]	18.00	6.20	—	273-600	16.98	10	7.77	79.03
$CHCl_3$(g)	7.052	35.598	−21.686	273-773	15.68	−24.2	−16.39	70.72
CHF_3(g)	3.616	18.239	−2.035	298-600	12.20	−167.0	−158.77	62.04
CH_2Br_2(g)[b]	14.80	7.60	—	273-600	13.0	1	0.66	70.1
CH_2ClF(g)	4.292	27.025	−10.605	250-600	11.24	−61.5	−55.45	63.17
CH_2Cl_2(g)	—	—	—	—	12.18	−22.95	−16.50	64.55
CH_2F_2(g)	4.203	21.633	4.088	250-600	10.25	−106.5	−99.92	58.94

Appendix 2 (continued)

Substance	Heat capacity					ΔH°_{298}, kcal/mol	ΔG°_{298}, kcal/mol	S°_{298}, e.u.
	Coefficients of equation $C_p = \varphi(T)$			Recommended temperature interval, K	$(C_p^\circ)_{298}$, cal/mol·K			
	a	$b \times 10^3$	$-c \times 10^6$					
$CH_3Br(g)$[c]	10.70	8.50	—	273-1200	10.15	−8.96	−6.70	58.76
$CH_3Cl(g)$	3.562	22.998	−7.541	273-773	9.74	−20.6	−15.00	56.02
$CH_3F(g)$	—	—	—	—	8.96	−59	−53.29	53.25
$CH_3I(g)$	4.105	24.487	−9.733	298-600	10.54	3.5	3.91	60.67
$CCl_3F(g)$	—	—	—	—	18.65	−66.5	−57.0	74.02
$CF_4(g)$	—	—	—	—	14.61	−223.0	−212.33	62.47
$(NH_2)_2CO(c)$, urea	—	—	—	—	22.26	−79.53	−47.02	25.00
$C_2H_5Cl(g)$	—	—	—	—	15.01	−25.7	−13.36	65.99
$C_6H_5Cl(lq)$	—	—	—	—	34.8	2.58	21.32	50.0
$C_6H_7N(lq)$, aniline	—	—	—	—	45.6	7.43	35.63	45.72
$C_6H_5NO_2(lq)$, nitrobenzene	—	—	—	—	44.4	3.8	34.95	53.6
$C_6H_6O(c)$, phenol	—	—	—	—	32.2	−39.44	−12.05	34.42

Note: The coefficient $c' \times 10^{-5}$ of the equation $C_p = \varphi(T)$ equals: [a] −2.46; [b] −2.50; [c] −2.70.

IV. Ions

Ion	ΔH°_{298}, kcal/g-ion	ΔG°_{298}, kcal/g-ion	S°_{298}, e.u.	Ion	ΔH°_{298}, kcal/g-ion	ΔG°_{298}, kcal/g-ion	S°_{298}, e.u.
Ag^+	25.23	18.43	17.36	Cr^{3+}	−50.6	−48.74	−75.6
$Ag(CN)_2^-$	64.3	72.1	48.12	CrO_4^{2-}	−209.23	−172.29	11.0
Al^{3+}	−127.0	−117.59	−71.6	$Cr_2O_7^{2-}$	−353.45	−307.75	60.7
AsO_4^{3-}	−212.73	−155.10	−39.98	Cs^+	−61.68	−69.69	31.6
$AuCl_4^-$	−77.6	−56.17	61.6	Cu^+	17.4	12.0	−10.6
Ba^{2+}	−125.25	−130.86	2.1	Cu^{2+}	16.00	15.67	−22.16
Be^{2+}	−96.5	−91.1	47.0	$Cu(NH_3)_2^{2+}$	−33.51	−7.29	28.14
Br^-	−29.02	−24.88	19.9	$Cu(NH_3)_4^{2+}$	−82.82	−26.65	67.04
BrO_3^-	−19.8	0.44	39.4	F^-	−79.79	−66.92	−3.35
CN^-	36.0	41.01	23.05	Fe^{2+}	−20.82	−18.86	−31.28
CO_3^{2-}	−161.84	−126.17	−13.6	Fe^{3+}	−11.08	−1.08	−73.84
$C_2O_4^{2-}$	−193.3	−159.55	19.1	Ga^{3+}	−50.6	−38.74	−76.8
Ca^{2+}	−129.7	−132.10	−13.2	H^+	0	0	0
Ce^{3+}	−166.8	−161.5	−48.0	$HAsO_4^{2-}$	−217.08	−171.04	1.11
Cd^{2+}	−18.0	−18.56	−16.95	HCO_3^-	−165.39	−140.26	21.8
Cl^-	−39.94	−31.37	13.51	$HCrO_4^-$	−208.53	−181.16	43.1
ClO^-	−26.3	−8.75	7.88	HPO_4^{2-}	−307.4	−258.9	−8.0
ClO_2^-	−15.9	4.1	24.2	HS^-	−4.1	2.83	15.58
ClO_3^-	−22.84	−0.05	39.3	HSO_3^-	−150.47	−126.17	30.83
ClO_4^-	−29.54	− 0.81	43.9	HSO_4^-	−212.53	−180.92	30.82
Co^{2+}	−13.53	−12.82	−26.4	HSe^-	4.2	11.52	16.71

Appendix 2 (concluded)

Ion	ΔH°_{298}, kcal/g-ion	ΔG°_{298}, kcal/g-ion	S°_{298}, e.u.	Ion	ΔH°_{298}, kcal/g-ion	ΔG°_{298}, kcal/g-ion	S°_{298}, e.u.
$HSeO_3^-$	−122.5	−98.26	33.47	Ni^{2+}	−12.7	−10.89	−30.13
$HSeO_4^-$	−137.7	−108.5	41.34	OH^-	−54.98	−37.60	−2.60
$H_2AsO_4^-$	−217.85	−180.59	28.34	PO_4^{3-}	−303.90	−242.02	−52.92
$H_2PO_4^-$	−308.29	−268.72	21.9	Pb^{2+}	0.33	−5.83	2.7
Hg^{2+}	41.46	39.36	−6.01	$PtCl_6^{2-}$	−161	−117	52.6
Hg_2^{2+}	41.05	36.71	19.64	Rb^+	−60.00	−67.77	28.8
In^{3+}	−32.5	−23.4	−63.4	S^{2-}	7.8	20.41	−3.47
I^-	−13.2	−12.35	26.63	SO_3^{2-}	−153.2	−116.34	11.30
IO_3^-	−55.9	−33.81	28.9	SO_4^{2-}	−217.73	−178.22	4.3
I_3^-	−12.2	−12.34	57.71	$S^2O_3^{2-}$	−159	−123.5	0.90
K^+	−60.29	−67.53	24.12	$S_4O_6^{2-}$	−299	−246.3	62
La^{3+}	−169.0	−164.0	−50.0	Sc^{3+}	−151.02	−143.7	−63.2
Li^+	−66.55	−68.86	2.5	Se^{2-}	17.7	32.0	−6.70
Mg^{2+}	−110.36	−108.81	−28.6	SeO_3^{2-}	−121.3	−86.90	0.61
Mn^{2+}	−52.7	−54.96	−16.0	SeO_4^{2-}	−143.3	−106.24	14.98
Mn^{3+}	−24.0	−20.4	−51	Sn^{2+}	−5.83	−6.48	−16.7
MnO_4^-	−127.4	−105.23	46.9	Sr^{2+}	−133.0	−136.58	−6.5
NH_4^+	−31.63	−19.00	27.32	Tl^+	1.54	−7.75	30.9
NO_2^-	−25.0	−8.86	33.35	Tl^{3+}	47.0	51.3	−46.0
NO_3^-	−49.57	−26.67	35.18	U^{4+}	−141.1	−131.5	−82.6
Na^+	−57.46	−62.65	14.08	Zn^{2+}	−36.72	−35.17	−25.43

APPENDIX 3

CORRECTIONS FOR THE APPROXIMATE CALCULATION OF THE STANDARD HEATS OF FORMATION, HEAT CAPACITIES AND ENTROPIES FOR THE IDEALIZED GASEOUS STATE [C10]

A. Properties of Basic Substances

Substance	ΔH°_{298}, kcal/mol	Coefficients of equation $C_p = \varphi(T)$			S°_{298}, e.u.
		a	$b \times 10^3$	$c \times 10^6$	
Methane	−17.89	3.79	16.62	−3.24	44.50
Cyclopentane	−18.46	−9.02	109.28	−40.23	70.00
Cyclohexane	−29.43	−11.53	139.65	−52.02	71.28
Benzene	19.82	−4.20	91.30	−36.63	64.34
Naphthalene	35.40	3.15	109.40	−34.79	80.70
Methylamine	− 7.10	4.02	30.72	−8.70	57.70
Dimethylamine	− 7.80	3.92	48.31	−14.09	65.20
Trimethylamine	−10.90	3.93	65.85	−19.48	—
Dimethyl ether	−46.00	6.42	39.64	−11.45	63.70
Formamide	−49.50	6.51	25.18	−7.47	—

B. Corrections for Substitution of the Primary Hydrogen Atom by CH_3 Groups

Basic group	$\Delta(\Delta H^\circ_{298})$, kcal/mol	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	ΔS°_{298}, e.u.
Methane	−2.50	−2.00	23.20	−9.12	10.35
Cyclopentane					
first substitution	−7.04	1.87	17.55	−6.68	11.24
second substitution * :					
1,1	−7.55	−0.67	24.29	−10.21	4.63
1,2 (*cis*)	−5.46	−0.01	22.69	−9.46	6.27
1,2 (*trans*)	−7.17	0.28	21.97	−9.18	6.43
1,3 (*cis*)	−6.43	0.28	21.97	−9.18	6.43
1,3 (*trans*)	−6.97	0.28	21.97	−9.18	6.43
Cyclohexane					
first substitution	−7.56	2.13	18.66	−5.71	10.78
second substitution * :					
1,1	−6.27	−2.14	25.69	−10.09	5.18
1,2 (*cis*)	−4.16	−0.65	22.19	−8.84	7.45

* The additional correction $\Delta(\Delta H^\circ_{298})$ for each following substitution equals 7.00 kcal/mol.

Appendix 3 (continued)

Basic group	$\Delta(\Delta H^\circ_{298})$, kcal/mol	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	ΔS°_{298}, e.u.
1,2 (*trans*)	−6.03	−0.06	22.59	−2.56	6.59
1,3 (*cis*)	−7.18	−0.34	21.49	−7.95	6.48
1,3 (*trans*)	−5.21	0.29	19.29	−7.23	7.86
1,4 (*cis*)	−5.23	0.29	19.29	−7.23	6.48
1,4 (*trans*)	−7.13	−0.72	23.79	−9.91	5.13
correction for increase of ring for each added carbon atom	−10.97	−2.51	30.37	−11.79	1.28
Benzene					
first substitution	−7.87	0.78	16.68	−5.41	12.08
second substitution:					
1,2	−7.41	4.27	9.72	−1.87	7.89
1,3	−7.83	0.77	17.46	−6.19	9.07
1,4	−7.66	1.76	13.45	−3.41	7.81
third substitution:					
1,2,3	−6.83	1.41	12.78	−2.71	9.19
1,2,4	−7.87	1.61	12.72	−2.77	10.42
1,3,5	−7.96	2.41	11.30	−1.90	6.66
Naphthalene					
first substitution	−4.50	0.36	17.65	−5.88	12.00
second substitution:					
1,2	−6.30	5.20	6.02	−1.18	8.10
1,3	−6.50	1.72	14.18	−3.76	9.20
1,4	−8.00	1.28	14.57	−3.98	7.80
Methylamine	−5.70	−0.10	17.52	−5.35	—
Dimethylamine	−6.30	−0.10	17.52	−5.35	—
Trimethylamine	−4.10	−0.10	17.52	−5.35	—
Formamide					
substitution of H at carbon atom	−9.00	6.11	−1.75	4.75	—

C. Corrections for Substitution of the Secondary Hydrogen Atom by CH_3 Groups

(A)	(B)	$\Delta(\Delta H^\circ_{298})$, kcal/mol	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	ΔS°_{298}, e.u.
1	1	−4.75	0.49	22.04	−8.96	10.10
1	2	−4.92	1.09	17.79	−6.47	9.18
1	3	−4.42	1.00	19.88	−8.03	9.72

Appendix 3 (continued)

(A)	(B)	$\Delta(\Delta H^\circ_{298})$, kcal/mol	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	ΔS°_{298}, e.u.
1	4	−5.0	1.39	17.12	−5.88	11.00
1	5	−4.68	1.09	18.71	−7.16	10.76
2	1	−6.31	−0.30	21.74	−8.77	5.57
2	2	−6.33	−0.64	23.38	−9.97	7.15
2	3	−5.25	0.80	19.27	−7.70	6.53
2	4	−3.83	2.52	16.11	−5.88	7.46
2	5	−6.18	0.37	19.25	−7.72	6.72
3	1	−8.22	−0.28	24.21	−10.49	2.81
3	2	−7.00	−0.93	24.73	−8.95	3.87
3	3	−5.19	−3.27	30.96	−14.06	3.99
3	4	−4.94	−0.14	27.57	−10.27	1.88
3	5	−9.20	0.42	16.20	−4.68	1.30
In esters or ethers (1−0)		−7.00	−0.01	17.58	−5.33	14.00
Substitution of H in carboxylic group by CH_3 with formation of ester		9.50	0.44	16.63	−4.95	16.70

D. Corrections for Substitution of Single Bonds by Multiple Ones

Kind of bond	$\Delta(\Delta H^\circ_{298})$, kcal/mol	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	ΔS°_{298}, e.u.
1=1	32.88	0.21	−8.28	1.36	−2.40
1=2	30.00	1.12	−11.40	3.32	−0.21
1=3	28.23	2.18	−15.62	6.42	−0.11
2=2 (*cis*)	28.39	−3.57	0.14	1.08	−1.19
2=2 (*trans*)	27.40	1.27	−12.77	3.88	−2.16
2=3	26.72	−2.02	−10.42	3.83	−0.28
3=3	25.70	−0.41	−15.14	6.39	−0.66
1≡1	74.58	4.72	−24.36	6.29	−9.85
2≡2	65.50	1.00	−25.70	−9.50	−3.97
1≡2	69.52	3.16	−26.37	8.82	−4.19

E. Additional Corrections for Final Structure of Hydrocarbons

	$\Delta(\Delta H^\circ_{298})$, kcal/mol	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	ΔS°_{298}, e.u.
Additional correction for each long side chain in ring: more than 2C in side chain of cyclopentane	−0.45	−0.48	1.50	1.15	0.12

Appendix 3 (concluded)

	$\Delta(\Delta H^\circ_{298})$, kcal/mol	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	ΔS°_{298}, e.u.
more than 2C in side chain of cyclohexane	0.32	0.76	2.10	1.30	−0.39
more than 4C in side chain of benzene	−0.70	0.22	−0.20	0.08	−0.62
Additional correction for double bond introduced :					
for conjugated bonds	13.16	2.24	1.16	−0.25	−3.74
for alternating bonds	−4.28	−0.94	3.88	−3.49	−5.12
for double bond adjacent to aromatic ring :					
in side chain less than 5C long	−2.00	1.01	−3.24	1.31	−2.65
in side chain over 4C long	−1.16	1.01	−3.24	1.31	−2.65

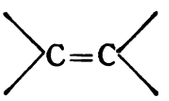
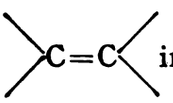
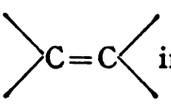
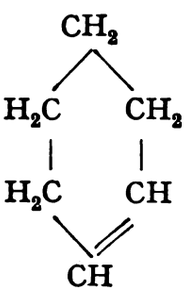
F. Corrections for Groups Substituting CH_3

Group	$\Delta(\Delta H^\circ_{298})$, kcal/mol	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	ΔS°_{298}, e.u.
−OH (aliphatic, meta, para)	−32.70	3.17	−14.86	5.59	2.60
−OH (ortho)	−47.70	—	—	—	—
$-NO_2$	1.20	6.30	−19.53	10.63	2.00
−CN	39.00	3.64	−13.92	4.53	4.00
−Cl; for the first Cl at a carbon atom	0	2.19	−18.85	6.26	0
−Cl; for each following one	4.50	—	—	—	—
−Br	10.00	2.81	−19.41	6.33	3.00*
−F	−35.00	2.24	−23.61	11.79	−1.00*
−I	24.80	2.73	−17.37	4.09	5.00*
=O (aldehyde)	−12.90	3.61	−55.72	22.72	−12.30
−COOH	−87.00	8.50	−15.07	7.94	15.40
=O (ketone)	−13.20	5.02	−66.08	30.21	−2.40
−SH	15.80	4.07	−24.96	12.37	5.20
$-C_6H_5$	32.30	−0.79	53.63	−19.21	21.70
$-NH_2$	12.30	1.26	−7.32	2.23	−4.80

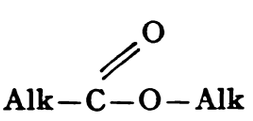
* The corrections for the entropy of halogens calculated for methyl derivatives should be increased by unity. For example, the entropy of methyl chloride is 44.4 (basic group) + 10.4 (substitution of the primary hydrogen atom by a $-CH_3$ group) + 0 (substitution by chlorine) + 1.

APPENDIX 4

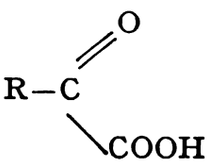
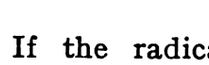
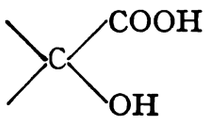
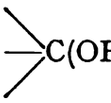
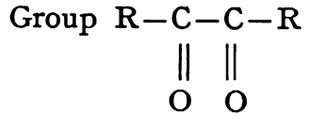
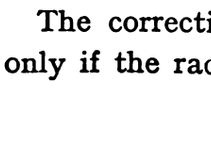
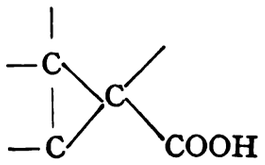
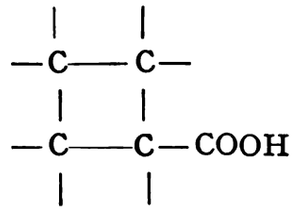
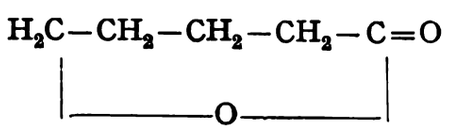
HEAT CORRECTIONS FOR THE KHARASCH EQUATION [EQ. (3.5)] [C13]

Nature of groups, substituents and bonds	Heat correction Δ_i, kcal/mol	Remarks
Bond between aliphatic and aromatic radicals Alk—Ar	3.5	Upon combustion of the carbon atoms, one of which belongs to an aromatic and the other to an aliphatic radical, all the electrons belonging to these atoms will migrate; $n_e = 0$
Bond between aromatic radicals Ar—Ar	6.5	Upon combustion, all the electrons belonging to the carbon atoms migrate. The number of structural heat corrections for polycyclic compounds equals the number of "junctions" of the nuclei
Double bond 	−13.0	
Double bond  in *cis*-compounds	−16.5	
Double bond  in *trans*-compounds	−13.0	
Bond between aromatic radical and vinyl Ar—CH=CH_2 or acetyl Ar—C≡CH radicals	6.5	
Double bond in closed ring 	−6.5	
Triple bond —C≡CH	−46.1	
Group —C≡C— not bound to hydrogen	−33.1	

Appendix 4 (continued)

Nature of groups, substituents and bonds	Heat correction Δi, kcal/mol	Remarks
Bond between primary aliphatic radical and hydroxyl group (primary alcohol)	−13	Upon combustion of the carbon bound to a hydroxyl group, only three and not all of the electrons migrate. The electron participating in the formation of a bond between carbon and oxygen, and also that of the hydrogen in the hydroxyl group do not migrate; $n_e = 2$
Bond between secondary aliphatic radical and hydroxyl group (secondary alcohol)	−6.5	Ditto
Bond between tertiary aliphatic radical and hydroxyl group (tertiary alcohol)	−3.5	Ditto
Bond between aromatic radical and hydroxyl group	−3.5	The same as for aliphatic alcohols
Aliphatic and aromatic ethers Alk(Ar)−O−(Ar)Alk	−19.5	Only two electrons of the carbon bound to the oxygen migrate upon combustion; $n_e = 2$
Aliphatic esters 	−16.5	$n_e = 4$
Aldehyde group in aliphatic and aromatic compounds	−13	In the aldehyde group, two electrons of the carbon bound to the oxygen migrate upon combustion; $n_e = 2$
Ketone group in aliphatic and aromatic compounds	−6.5	Ditto

Appendix 4 (continued)

Nature of groups, substituents and bonds	Heat correction Δ_i, kcal/mol	Remarks
α-Keto-acids 	−13	If the radical  is bound to the group — COOH, the indicated correction is introduced for this bond; in general the group — COOH does not require such a correction. Upon combustion, only one of the electrons belonging to the carbon of the carboxyl group migrates
Hydroxy-acids 	−6.5	The correction is introduced only in case of a bond of the radical  to the group —COOH. For the remaining cases see α-keto-acids
Group 	−13	The correction is introduced only if the radical  is bound to a similar one
Trimethylene rings in carboxylic acids 	−13	
Cyclobutane rings in carboxylic acids 	−13	
Lactones of the type 	−13	

Appendix 4 (continued)

Nature of groups, substituents and bonds	Heat correction Δt, kcal/mol,	Remarks
Carboxylic acid anhydrides	−10	
Primary aliphatic amines Alk−NH_2	−13	Upon combustion, all the electrons belonging to the carbon bound to the aminogroup migrate. When calculating the number of migrating electrons, the electrons belonging to the hydrogen directly bound to the nitrogen are also taken into account
Secondary aliphatic amines Alk−NH−Alk	−19.5	Ditto
Tertiary aliphatic amines Alk−N(−Alk)−Alk	−26	Ditto
Primary aromatic amines Ar−NH_2	−6.5	Ditto
Secondary aromatic amines Ar−NH−Ar	−13	Ditto
Tertiary aromatic amines Ar−N(−Ar)−Ar	−19.5	Ditto. Fatty-aromatic tertiary amines are considered tertiary aromatic
Substituted amines of the type >N−C(=O)−Ar and −NH−N<	−6.5	
Acetylated aromatic amines Ar−NH−C(=O)−CH_3	−3.5	
Bond between carbon and the nitrile group −C≡N in aliphatic and aromatic compounds	−16.5	Upon combustion, all four electrons of the carbon bound to the nitrogen in the nitrile group migrate

Appendix 4 (concluded)

Nature of groups, substituents and bonds	Heat correction Δi, kcal/mol,	Remarks
Aromatic nitriles	6.5	Two corrections are introduced when calculating ΔH_{comb}: for the bond between carbon and the group $-C\equiv N$ and to take into account the presence of the nitrile group itself
Isonitrile group Alk—N=C< in an aliphatic series	—33.1	
Nitrogroup $-NO_2$ in aliphatic and aromatic compounds	—13	Upon combustion, all but one of the electrons of the carbon bound to the nitrogroup migrate; this electron remains with the nitrogen of the nitrogroup which is reduced in the process of combustion; $n_e = 1$
Chlorine in aliphatic compounds Alk—Cl	—13	$n_e = 1$
Bromine in aromatic compounds Ar—Br	—13	$n_e = 1$
Chlorine in aromatic compounds Ar—Cl	—6.5	Upon combustion of halogen-containing compounds, all but one of the electrons of the carbon atom bound to the halogen migrate; $n_e = 1$
Bromine in aliphatic compounds Alk—Br	—13	Ditto
Iodine in aromatic compounds Ar—I	—40.1	Ditto
Iodine in aliphatic compounds Alk —I	—40.1	Ditto
Sulphogroup in aliphatic compounds Alk—SO_3H	23.4	
Quinones	—33.1	

APPENDIX 5

THERMODYNAMIC QUANTITIES FOR A SIMPLE HARMONIC OSCILLATOR IN ONE DIMENSION (EINSTEIN FUNCTIONS)

$\frac{\Theta}{T}$	$\ln Q_{vib}$	C	$\frac{U-U_0}{T}=\frac{1}{T}\int_0^T C\,dT$	S	$-\frac{G-U_0}{T}=\int_0^T \frac{dT}{T^2}\int_0^T C\,dT$
0	—	1.986	1.986	∞	∞
0.10	—	1.983	1.888	6.560	4.67
0.15	—	1.981	1.841	5.730	3.89
0.20	—	1.979	1.761	5.190	3.39
0.25	—	1.976	1.747	4.740	2.99
0.30	—	1.974	1.702	4.390	2.68
0.35	—	1.967	1.659	4.080	2.42
0.40	—	1.960	1.615	3.820	2.20
0.45	—	1.952	1.572	3.600	2.02
0.50	—	1.945	1.531	3.380	1.85
0.55	0.8603	1.938	1.490	3.200	1.709
0.60	0.7959	1.928	1.449	3.031	1.581
0.65	0.7382	1.918	1.410	2.877	1.467
0.70	0.6863	1.908	1.371	2.736	1.364
0.75	0.6394	1.896	1.334	2.604	1.270
0.80	0.5966	1.884	1.297	2.482	1.185
0.85	0.5576	1.871	1.260	2.369	1.108
0.90	0.5218	1.858	1.224	2.262	1.037
0.95	0.4890	1.844	1.191	2.162	0.972
1.00	0.4587	1.829	1.156	2.068	0.911
1.05	0.4307	1.814	1.123	1.979	0.856
1.10	0.4048	1.798	1.090	1.895	0.804
1.15	0.3807	1.782	1.058	1.815	0.756
1.20	0.3584	1.765	1.027	1.740	0.712
1.25	0.3376	1.747	0.997	1.668	0.671
1.30	0.3182	1.729	0.968	1.600	0.632
1.35	0.3001	1.711	0.939	1.535	0.596

Appendix 5 (continued)

$\frac{\Theta}{T}$	$\ln Q_{vib}$	C	$\frac{U-U_0}{T}=\frac{1}{T}\int_0^T C\,dT$	S	$-\frac{G-U_0}{T}=\int_0^T\frac{dT}{T^2}\int_0^T C\,dT$
1.40	0.2832	1.692	0.911	1.437	0.563
1.45	0.2673	1.673	0.883	1.414	0.531
1.50	0.2525	1.659	0.856	1.358	0.502
1.55	0.2386	1.633	0.829	1.304	0.474
1.60	0.2255	1.612	0.804	1.252	0.448
1.65	0.2132	1.592	0.779	1.203	0.424
1.70	0.2017	1.570	0.755	1.156	0.401
1.75	0.1909	1.549	0.731	1.111	0.379
1.80	0.1807	1.527	0.708	1.067	0.359
1.85	0.1711	1.505	0.686	1.026	0.340
1.90	0.1620	1.483	0.664	0.986	0.322
1.95	0.1535	1.461	0.633	0.948	0.305
2.00	0.1454	1.439	0.622	0.911	0.289
2.10	0.1306	1.393	0.582	0.842	0.259
2.20	0.1174	1.348	0.545	0.778	0.233
2.30	0.1056	1.302	0.510	0.719	0.210
2.40	0.0951	1.256	0.476	0.665	0.189
2.50	0.0857	1.210	0.444	0.614	0.170
2.60	0.0772	1.164	0.414	0.568	0.153
2.70	0.0696	1.119	0.386	0.525	0.138
2.80	0.0627	1.074	0.360	0.485	0.125
2.90	0.0566	1.030	0.336	0.448	0.112
3.00	0.0511	0.986	0.312	0.414	0.102
3.10	0.0461	0.943	0.291	0.382	0.092
3.20	0.0416	0.901	0.270	0.353	0.083
3.30	0.0376	0.860	0.251	0.326	0.075
3.40	0.0339	0.820	0.233	0.301	0.067
3.50	0.0307	0.781	0.217	0.277	0.061

Appendix 5 (concluded)

$\frac{\Theta}{T}$	$\ln Q_{vib}$	C	$\frac{U-U_0}{T}=\frac{1}{T}\int_0^T C\,dT$	S	$-\frac{G-U_0}{T}=\int_0^T \frac{dT}{T^2}\int_0^T C\,dT$
3.60	0.0277	0.744	0.201	0.256	0.055
3.70	0.0250	0.707	0.187	0.236	0.050
3.80	0.0226	0.672	0.173	0.218	0.045
3.90	0.0205	0.637	0.160	0.201	0.041
4.00	0.0185	0.604	0.148	0.185	0.037
4.20	0.0151	0.542	0.127	0.157	0.030
4.40	0.0124	0.484	0.109	0.133	0.025
4.60	0.0101	0.431	0.0927	0.113	0.020
4.80	0.0083	0.383	0.0790	0.096	0.016
5.00	0.0068	0.339	0.0673	0.081	0.014
5.20	0.0055	0.300	0.0573	0.068	0.011
5.40	0.0045	0.262	0.0487	0.058	0.009
5.60	0.0037	0.232	0.0413	0.049	0.007
5.80	0.0030	0.204	0.0353	0.041	0.006
6.00	0.0025	0.178	0.0297	0.035	0.005
6.40	0.0016	0.136	0.0251	0.024	0.003
6.80	0.0011	0.103	0.0151	0.017	0.002
7.20	0.0007	0.077	0.0107	0.014	0.001
7.60	0.0005	0.057	0.0076	0.009	0.001
8.00	0.0003	0.0427	0.0053	0.006	0.001
8.40	0.0002	0.032	0.0038	0.004	0.000
8.80	0.0002	0.023	0.0030	0.003	—
9.20	0.0001	0.017	0.0018	0.002	—
9.60	0.0001	0.012	0.0013	0.001	—
10.0	—	0.009	0.0009	0.001	—
11	—	0.004	0.0004	—	—
12	—	0.0017	0.0001	—	—
13	—	0.0007	—	—	—

APPENDIX 6

TARASOV AND DEBYE FUNCTIONS

A. Tarasov Functions *

$\frac{\Theta}{T}$	C_1									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	5.958	5.953	5.938	—	5.910	—	5.886	—	5.846	—
1	5.793	5.774	5.726	5.695	5.651	5.618	5.666	5.517	5.472	5.421
2	5.368	5.319	5.261	5.208	5.152	5.093	5.038	4.970	4.916	4.865
3	4.791	4.733	4.660	4.601	4.540	4.481	4.416	4.359	4.299	4.246
4	4.182	4.123	4.068	4.013	3.953	3.901	3.844	3.795	3.739	3.689
5	3.640	3.592	3.542	3.494	3.442	3.383	3.345	3.287	3.249	3.206
6	3.166	3.117	3.074	3.030	2.989	2.948	2.909	2.870	2.831	2.793

$\frac{\Theta}{T}$	C_2									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	5.95[illegible]	5.957	5.952	—	5.902	—	5.846	—	5.79	—
1	5.73	5.70	5.63	5.56	5.51	5.44	5.38	5.30	5.24	5.16
2	5.09	5.01	4.93	4.84	4.77	4.68	4.60	4.51	4.43	4.34
3	4.25	4.17	4.07	3.98	3.90	3.82	3.74	3.66	3.57	3.49
4	3.41	3.33	3.24	3.18	3.09	3.02	2.95	2.88	2.81	2.74
5	2.68	2.61	2.54	2.49	2.42	2.37	2.30	2.24	2.19	2.15
6	2.09	2.04	1.98	1.95	1.89	1.85	1.80	1.76	1.72	1.69

$\frac{\Theta}{T}$	C_1	C_2	$\frac{\Theta}{T}$	C_1	C_2	$\frac{\Theta}{T}$	C_1	C_2
7	2.758	1.65	10	1.961	0.860	16	1.226	0.336
8	2.458	1.34	12	1.634	0.597	18	1.089	0.265
9	2.175	1.061	14	1.401	0.439	20	0.981	0.215

* For greater details see Chernoplekov, N. A. *Zh. fiz. khim.*, **25**: 878ff (1951). For the values of the Tarasov functions needed to calculate other properties see Chernoplekov, N.A. *Zh. fiz. khim.*, **27**: 1090-1102 (1953).

B. Debye Functions

$\frac{\Theta}{T}$	C_V									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	5.961	5.96	5.95	5.94	5.92	5.89	5.86	5.82	5.78	5.74
1	5.676	5.62	5.55	5.49	5.42	5.35	5.27	5.19	5.10	5.01
2	4.919	4.83	4.74	4.65	4.55	4.44	4.34	4.24	4.14	4.04

Appendix 6 (continued)

$\frac{\Theta}{T}$	C_V									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
3	3.945	3.84	3.74	3.65	3.55	3.45	3.36	3.27	3.18	3.09
4	2.999	2.91	2.83	2.75	2.67	2.59	2.51	2.43	2.35	2.27
5	2.200	2.13	2.06	2.00	1.94	1.88	1.82	1.76	1.70	1.64
6	1.583	1.53	1.48	1.43	1.38	1.34	1.30	1.26	1.22	1.18
7	1.138	1.103	1.068	1.034	1.001	0.969	0.938	0.908	0.880	0.854
8	0.831	0.811	0.791	0.771	0.751	0.732	0.713	0.694	0.675	0.656
9	0.637	0.618	0.599	0.580	0.561	0.542	0.524	0.506	0.487	0.469
10	0.451	0.435	0.421	0.40.	0.398	0.388	0.378	0.368	0.359	0.351
11	0.343	0.335	0.327	0.319	0.311	0.303	0.295	0.287	0.280	0.273
12	0.267	0.261	0.255	0.249	0.243	0.237	0.231	0.225	0.220	0.215
13	0.210	0.205	0.200	0.196	0.192	0.188	0.184	0.180	0.176	0.172
14	0.168	0.164	0.161	0.158	0.155	0.152	0.149	0.146	0.143	0.140
15	0.137	0.134	0.131	0.128	0.125	0.123	0.121	0.119	0.117	0.115

$\frac{\Theta}{T}$	C_V	$\frac{\Theta}{T}$	C_V	$\frac{\Theta}{T}$	C_V	$\frac{\Theta}{T}$	C_V	$\frac{\Theta}{T}$	C_V
16	0.113	19	0.067	22	0.0433	25	0.0296	28	0.0211
17	0.094	20	0.058	23	0.0380	26	0.0262	29	0.0189
18	0.079	21	0.0499	24	0.0335	27	0.0234	30	0.0172

$$\frac{U - U_0}{T} = \frac{1}{T}\int_0^T C_V \, dT$$

$\frac{\Theta}{T}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	5.961	5.739	5.526	5.317	5.115	4.917	4.726	4.540	4.362	4.190
1	4.021	3.858	3.699	3.549	3.402	3.262	3.126	2.995	2.867	2.742
2	2.626	2.516	2.409	2.307	2.207	2.110	2.019	1.931	1.846	1.766
3	1.689	1.615	1.544	1.477	1.413	1.353	1.295	1.239	1.185	1.133
4	1.083	1.037	0.994	0.953	0.913	0.874	0.837	0.801	0.766	0.732
5	0.702	0.672	0.644	0.619	0.595	0.571	0.548	0.526	0.504	0.483
6	0.462	0.444	0.426	0.409	0.393	0.379	0.366	0.352	0.339	0.326
7	0.313	0.302	0.291	0.281	0.270	0.261	0.252	0.242	0.234	0.227
8	0.220	0.214	0.208	0.202	0.196	0.191	0.186	0.180	0.175	0.169
9	0.164	0.159	0.154	0.149	0.144	0.138	0.134	0.129	0.124	0.120
10	0.1150	0.1108	0.1071	0.1039	0.1010	0.0984	0.0958	0.0932	0.0908	0.0887
11	0.0867	0.0846	0.0825	0.0805	0.0784	0.0764	0.0743	0.0723	0.0705	0.0687
12	0.0672	0.0656	0.0641	0.0626	0.0611	0.0596	0.0581	0.0566	0.0553	0.0540
13	0.0527	0.0515	0.0503	0.0491	0.0481	0.0471	0.0461	0.0451	0.0441	0.0431
14	0.0420	0.0411	0.0403	0.0395	0.0388	0.0380	0.0373	0.0365	0.0358	0.0350
15	0.0343	0.0335	0.0328	0.0320	0.0313	0.0308	0.0303	0.0298	0.0293	0.0288

Appendix 6 (concluded)

$\frac{\Theta}{T}$	$-\frac{G-U_0}{T} = \int_0^T \frac{dT}{T^2} \int_0^T C_V\, dT$									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	—	15.93	12.02	9.82	8.32	7.20	6.320	5.605	5.011	4.508
1	4.081	3.699	3.368	3.079	2.822	2.593	2.386	2.201	2.033	1.880
2	1.743	1.617	1.503	1.399	1.302	1.214	1.133	1.058	0.990	0.926
3	0.8673	0.8130	0.7627	0.7164	0.6738	0.6330	0.5960	0.5618	0.5293	0.4997
4	0.4713	0.4453	0.4214	0.3989	0.3778	0.3580	0.3392	0.3215	0.3047	0.2888
5	0.2742	0.2608	0.2478	0.2363	0.2253	0.2148	0.2049	0.1953	0.1862	0.1773
6	0.1689	0.1611	0.1539	0.1471	0.1409	0.1352	0.1299	0.1247	0.1197	0.1147
7	0.1098	0.1056	0.1015	0.0975	0.0938	0.0902	0.0869	0.0836	0.0805	0.0777
8	0.0752	0.0731	0.0710	0.0690	0.0670	0.0650	0.0630	0.0610	0.0591	0.0573
9	0.0555	0.0537	0.0519	0.0501	0.0483	0.0466	0.0449	0.0433	0.0417	0.0401
10	0.0386	0.0371	0.0358	0.0348	0.0338	0.0329	0.0320	0.0311	0.0303	0.0296
11	0.0289	0.0282	0.0275	0.0268	0.0261	0.0254	0.0247	0.0241	0.0235	0.0229
12	0.0224	0.0218	0.0213	0.0208	0.0203	0.0198	0.0193	0.0188	0.0184	0.0180
13	0.0175	0.0171	0.0167	0.0164	0.0160	0.0157	0.0154	0.0150	0.0147	0.0144
14	0.0140	0.0137	0.0134	0.0132	0.0129	0.0126	0.0124	0.0122	0.0119	0.0117

APPENDIX 7

VALUES OF CHARACTERISTIC TEMPERATURES FOR SELECTED GASES *

Gas	Θ	Gas	Θ_1	Θ_2	Θ_3
Br_2	461	CCl_4	341 (2)	440 (3)	630
CO	3085	CH_4	1870 (3)	2170 (2)	4320 (3)
Cl_2	801	COS	746 (3)	1230	2936
F_2	1533	CO_2	960 (2)	1830	3380
HBr	4200	CS_2	568 (2)	939	2194
HCl	4130	C_2H_2	859 (2)	1044 (2)	2838
HF	5790	C_2N_2	730 (2)	1060 (2)	1230 (2)
HI	3245	HCN	1020 (2)	2290	4710
H_2	6130	H_2O	2290	5730	5510
I_2	305	H_2S	1810	3750 (2)	—
NO	2705	NH_3	1357	2336 (2)	4176
N_2	3350	N_2O	844 (2)	1842	3195
O_2	2224	SO_2	750	1650	1950

* The temperature Θ_4 for CCl_4, CH_4, C_2H_2, C_2N_2, and NH_3 is 1114 (3), 4400, 4693 (3), 3080, 4776 (2), respectively. The temperature Θ_5 for C_2H_2 and C_2N_2 is 4826 and 3340, respectively.

APPENDIX 8

VALUES OF γ FOR τ FROM 1 TO 35

(a) Values for τ from 1 to 3.5

π \ τ	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	2.0	2.2	2.4	2.7	3.0	3.5
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
1	0.612	0.735	0.814	0.870	0.906	0.926	0.948	0.956	0.964	0.976	0.990	1.000	1.006	1.010	1.014
2	0.385	0.560	0.668	0.760	0.824	0.822	0.898	0.914	0.930	0.956	0.980	1.000	1.012	1.020	1.028
3	0.288	0.435	0.560	0.668	0.748	0.806	0.854	0.880	0.902	0.940	0.974	1.000	1.020	1.032	1.046
4	0.248	0.370	0.494	0.602	0.690	0.764	0.824	0.858	0.882	0.930	0.972	1.000	1.030	1.048	1.062
5	0.226	0.338	0.464	0.566	0.654	0.736	0.802	0.842	0.866	0.922	0.972	1.008	1.042	1.062	1.080
6	0.210	0.318	0.442	0.544	0.634	0.720	0.788	0.834	0.860	0.920	0.978	1.014	1.052	1.074	1.098
7	0.202	0.310	0.430	0.532	0.626	0.710	0.780	0.832	0.860	0.926	0.988	1.026	1.068	1.092	1.112
8	0.200	0.308	0.428	0.528	0.624	0.712	0.784	0.834	0.868	0.934	1.000	1.040	1.086	1.110	1.136
9	0.200	0.310	0.430	0.532	0.630	0.720	0.792	0.840	0.878	0.948	1.014	1.058	1.106	1.130	1.158
10	0.202	0.312	0.434	0.542	0.640	0.730	0.806	0.852	0.890	0.964	1.034	1.076	1.128	1.153	1.180
11	—	—	0.460	0.552	0.654	0.746	0.810	0.866	0.908	0.982	1.054	1.100	1.152	1.174	1.204
12	—	—	0.474	0.566	0.668	0.760	0.834	0.884	0.928	1.008	1.078	1.126	1.174	1.198	1.226
13	—	—	0.490	0.582	0.686	0.778	0.852	0.906	0.952	1.014	1.106	1.152	1.202	1.222	1.250
14	—	—	0.510	0.598	0.706	0.798	0.874	0.930	0.978	1.066	1.134	1.180	1.228	1.248	1.280
15	—	—	0.532	0.620	0.728	0.826	0.902	0.958	1.006	1.100	1.166	1.214	1.256	1.280	1.310
16	—	—	0.554	0.646	0.758	0.854	0.934	0.996	1.036	1.114	1.198	1.240	1.290	1.310	1.340
17	—	—	0.554	0.672	0.786	0.890	0.970	1.026	1.072	1.172	1.230	1.274	1.322	1.342	1.368
18	—	—	0.578	0.706	0.824	0.930	1.006	1.066	1.110	1.208	1.270	1.310	1.354	1.374	1.402
19	—	—	0.604	0.738	0.860	0.970	1.050	1.106	1.150	1.248	1.308	1.348	1.392	1.414	1.434
20	—	—	0.628	0.768	0.894	1.006	1.088	1.142	1.180	1.288	1.340	1.386	1.432	1.442	1.468
21	—	—	—	—	—	—	—	—	—	1.328	1.406	1.418	1.472	1.476	1.504
22	—	—	—	—	—	—	—	—	—	1.366	1.426	1.466	1.514	1.522	1.534

(b) Values for τ from 3.5 to 35

π \ τ	3.5	5	6	7	8	9	10	12	15	16	18	20	22	25	30	35
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
5	1.080	1.076	1.071	1.063	1.056	1.057	1.048	1.043	1.038	1.036	1.030	1.028	1.024	1.019	1.015	1.012
10	1.180	1.167	1.152	1.135	1.120	1.117	1.102	1.088	1.072	1.070	1.061	1.052	1.048	1.039	1.031	1.028
15	1.310	1.274	1.244	1.214	1.194	1.181	1.160	1.136	1.110	1.108	1.087	1.080	1.072	1.058	1.045	1.042
20	1.468	1.402	1.346	1.302	1.274	1.248	1.210	1.182	1.152	1.148	1.127	1.110	1.100	1.082	1.060	1.054
25	—	1.540	1.450	1.398	1.356	1.318	1.284	1.234	1.192	1.188	1.158	1.142	1.128	1.106	1.084	1.070
30	—	1.686	1.570	1.502	1.444	1.392	1.352	1.292	1.234	1.228	1.192	1.176	1.156	1.130	1.106	1.086
35	—	1.868	1.708	1.612	1.534	1.470	1.424	1.350	1.284	1.270	1.228	1.208	1.184	1.160	1.126	1.104
40	—	2.028	1.854	1.728	1.630	1.554	1.492	1.410	1.328	1.312	1.266	1.240	1.212	1.178	1.146	1.118
45	—	2.228	2.018	1.850	1.736	1.644	1.570	1.470	1.380	1.354	1.306	1.274	1.242	1.202	1.168	1.134
50	—	2.450	2.190	1.986	1.850	1.744	1.654	1.534	1.432	1.400	1.346	1.308	1.272	1.228	1.188	1.152
55	—	2.694	2.372	2.126	1.968	1.844	1.740	1.598	1.486	1.448	1.388	1.342	1.302	1.252	1.208	1.168
60	—	2.966	2.570	2.274	2.098	1.952	1.828	1.664	1.546	1.500	1.432	1.380	1.334	1.278	1.230	1.182
65	—	—	—	—	—	—	—	—	1.602	1.552	1.476	1.416	1.368	1.306	1.252	1.196
70	—	—	—	—	—	—	—	—	1.662	1.608	1.526	1.454	1.380	1.332	1.272	1.214
75	—	—	—	—	—	—	—	—	1.728	1.668	1.590	1.494	1.438	1.362	1.292	1.238
80	—	—	—	—	—	—	—	—	1.794	1.728	1.622	1.538	1.472	1.390	1.314	1.248
85	—	—	—	—	—	—	—	—	1.862	1.790	1.672	1.582	1.512	1.426	1.338	1.268
90	—	—	—	—	—	—	—	—	1.930	1.862	1.726	1.626	1.548	1.456	1.360	1.288
95	—	—	—	—	—	—	—	—	2.002	1.912	1.774	1.668	1.590	1.490	1.380	1.308
100	—	—	—	—	—	—	—	—	2.070	1.978	1.828	1.712	1.628	1.528	1.402	1.328

APPENDIX 9

CRITICAL PARAMETERS OF SELECTED LIQUIDS

Substance	t_{cr}	p_{cr}	V_{cr}
Elements, Simple Substances and Inorganic Compounds			
Ar	−122.5	48.0	75.2
He	−267.9	2.26	57.5
Kr	−63.8	54.3	92.3
Ne	−228.7	26.9	41.7
Xe	16.59	57.6	119.5
Br_2	311	102	135
Cl_2	144.0	76.1	124
F_2	−129	55	—
H_2	239.9	12.80	65.5
N_2	−149.9	38.5	92.1
O_2	−118.4	50.1	78
O_3	−12.1	54.6	89.4
$BiBr_3$	947	83	302
$BiCl_3$	905	118.1	261
CF_4	−45.4	36.9	136
C_2F_4	33	39.1	172
CO	−140.2	34.5	93
CO_2	31.0	72.9	94
$COCl_2$	182	56	190
CS_2	279	78.0	173
$GeCl_4$	279	38.0	330
HBr	89.8	84.0	—
HCN	183.5	53.2	139
HCl	51.4	81.5	86.8
HF	188	64.1	59
HI	150	81.1	—
H_2O	374.2	218.5	56

Appendix 9 (continued)

Substance	t_{cr}	p_{cr}	V_{cr}
H_2S	100.4	88.9	97.7
NH_3	132.3	111.3	73.1
NO	−93	64.6	58
NO_2	158	100	82
N_2O	36.4	71.6	97.3
N_2O_4	158	100	82
PF_3	−2.0	42.7	—
PH_3	51.3	64.5	—
SF_6	45.6	37.1	199
SO_2	157.5	77.8	122
SO_3	218	81	126
$SbCl_3$	520.9	—	271
$SiCl_4$	233	37.0	291
SiF_4	−14.1	36.7	—
SiF_3Cl	34.5	34.2	—
SiF_2Cl_2	95.8	34.5	—
$SiFCl_3$	165.3	35.5	—
SiH_4	−3	42.2	104
$SnCl_4$	318.7	37.0	351
Air	−140.9	37.2	—
	Organic Compounds		
CH_4	−82.6	45.7	100
C_2H_2	35.2	61.6	112
C_2H_4	9.2	50.0	124
C_2H_6	32.3	48.2	148
C_3H_6	91.8	45.6	181
C_3H_8	96.7	42.0	200
C_4H_6, butadiene-1,3	152	42.7	221
C_4H_8, butene-1	146.4	39.7	240
C_4H_8, butene-2	157	41	236

Appendix 9 (continued)

Substance	t_{cr}	p_{cr}	V_{cr}
C_4H_{10}	152.0	36.0	255
iso-C_4H_{10}	134.9	36.0	263
cyclo-C_5H_{10}	238.6	44.6	260
C_5H_{12}	196.6	33.3	311
iso-C_5H_{12}	187.8	32.9	308
C_5H_{12}, neopentane	160.6	31.57	303
C_6H_6	288.5	48.6	260
cyclo-C_6H_{12}	280	40	308
C_6H_{12}, methylcyclopentane	259.6	37.4	319
C_6H_{14}	234.7	29.9	368
$C_6H_5CH_3$	320.8	41.6	320
C_7H_{14}, methylcyclohexane	299.1	34.32	344
C_7H_{14}, ethylcyclopentane	296.3	33.5	375
C_7H_{16}	267.0	27.0	426
C_8H_{18}	296.7	24.6	490
C_9H_{12}, 1,2,4-trimethylbenzene	381.2	33	430
CHF_3	25.9	48	133
CH_2F_2	78.4	57.5	120
CH_2CF_2	29.7	44.0	155
CH_3CHF_2	113.5	44.3	181
CH_3CF_3	73.1	37.1	193
CH_3OH	240.0	78.5	118
C_2H_5OH	243.0	63	167
C_3H_7OH	264.0	50.2	220
CH_3OCH_3	126.9	53.0	193
$C_2H_5OC_2H_5$	194	35.6	280
$C_2H_5OC_3H_7$	227.	32.1	339
CH_3COCH_3	235.5	46.6	213
$C_2H_5COCH_3$	260	39.5	290

Appendix 9 (concluded)

Substance	t_{cr}	p_{cr}	V_{cr}
CH_3COOH	321.6	57.1	171
C_2H_5COOH	339	53	230
$HCOOCH_3$	214.0	59.2	172
$HCOOC_2H_5$	235.3	46.8	229
CH_3COOCH_3	233.7	46.3	228
$H_3CCOOC_3H_7$	264.9	40.1	285
$CH_3COOC_2H_5$	250.1	37.8	286
$CH_3COOC_3H_7$	276.2	32.9	345
CCl_4	238.1	45.0	276
CCl_3F	198.0	43.2	248
CCl_2F_2	111.5	39.6	218
$CClF_3$	28.8	39	180
$CHCl_3$	263.4	54	239
$CHCl_2F$	178.5	51.0	197
$CHClF_2$	96.4	48.5	165
CH_2Cl_2	237	60	180
CH_3Cl	143.1	65.9	143
CH_3F	44.6	58.0	113
CCl_3CF_3	214.1	33.7	325
C_2H_5Br	230.7	61.5	251
C_2H_5Cl	187.2	52	195
C_2H_5F	102.2	46.6	—
CH_2ClCH_2Cl	288	53	225
C_6H_5Br	397	44.6	343
C_6H_5Cl	359.2	44.6	308
C_6H_5F	286.6	44.6	271
C_6H_5I	448	44.6	351
$N(CH_3)_3$	160.1	40.2	254
$C_6H_5NH_2$	425.6	52.3	274

APPENDIX 10

ACTIVITY COEFFICIENTS FOR SELECTED ELECTROLYTES IN AQUEOUS SOLUTIONS AT $t = 25$ °C *

Electrolyte	γ at m =											
	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2	0.5	1	2	3
$AgNO_3$	—	—	—	—	—	—	0.734	0.657	0.536	0.429	0.316	0.252
$BaCl_2$	—	—	—	0.723	(0.66)	0.56	0.508	0.450	0.403	0.401	—	—
$CaCl_2$	—	—	—	—	—	—	0.518	0.472	0.448	0.500	0.792	1.483
$CdBr_2$	0.787	0.699	0.570	0.468	0.370	0.259	0.190	0.132	0.0780	0.0518	0.0361	0.0305
$CdCl_2$	0.819	0.743	0.623	0.524	0.456	0.304	0.228	0.1638	0.1006	0.0669	0.0441	0.0352
CdI_2	—	—	0.490	0.379	0.281	0.167	0.108	0.0685	0.0376	0.0251	0.0180	—
HBr	0.966	(0.954)	0.930	0.906	0.879	0.838	0.805	0.782	0.789	0.871	1.168	1.674
HCl	0.966	0.952	0.929	0.905	0.876	0.830	0.796	0.767	0.756	0.809	1.009	1.316
HNO_3	0.965	(0.953)	0.927	0.902	0.871	0.825	0.791	0.754	0.720	0.724	0.781	0.859
H_2SO_4	0.830	0.757	0.639	0.544	0.453	0.340	0.266	0.209	0.156	0.132	0.128	0.142
KBr	0.965	(0.953)	0.927	0.903	0.872	0.822	0.772	0.722	0.657	0.617	0.593	0.595
KCl	—	—	0.927	0.902	(0.87)	0.816	0.770	0.718	0.649	0.604	0.573	0.569
KI	—	—	—	—	—	—	0.778	0.733	0.676	0.645	0.637	0.652
KOH	—	—	—	—	—	—	0.776	0.739	0.712	0.735	0.863	1.051
$MgSO_4$	—	—	—	—	—	—	(0.150)	0.107	0.0675	0.0485	0.0417	0.0492
NaBr	0.966	(0.954)	0.930	0.906	0.879	0.838	0.782	0.741	0.697	0.683	0.731	0.812
NaCl	—	—	—	—	—	—	0.778	0.735	0.681	0.657	0.668	0.714
$NaNO_3$	—	—	—	—	—	—	0.762	0.703	0.617	0.548	0.478	0.437
NaOH	—	—	—	—	—	0.82	0.764	0.735	0.688	0.677	0.707	0.782
Na_2SO_4	—	—	—	—	—	0.53	0.452	0.371	0.270	0.204	0.1544	0.1387
$PbCl_2$	0.859	0.803	0.704	0.612	0.497	—	—	—	—	—	—	—
$ZnBr_2$	—	—	—	—	0.680	0.600	0.547	0.510	0.511	0.552	0.572	0.598
$ZnCl_2$	—	—	0.789	0.731	0.667	0.628	0.515	0.462	0.394	0.339	0.289	0.287
ZnI_2	—	0.851	0.799	0.746	0.690	0.621	0.581	0.559	0.610	0.800	1.028	1.123
$ZnSO_4$	0.700	0.608	0.477	0.387	0.298	0.202	0.150	0.104	0.0630	0.0435	0.0357	0.0408

* The values given in parentheses have been found by graphical interpolation, extrapolation or by comparative calculations.

Electrolyte	γ at m =											
	0.1	0.2	0.3	0.5	0.7	1.0	1.5	2.0	2.5	3	4	5
$AlCl_3$	(0.337)	0.305	0.302	0.331	0.388	0.539	—	(2.536)	(5.705)	(13.28)	—	—
$Al_2(SO_4)_3$	(0.0350)	0.0225	0.0175	0.0143	0 0142	0.0175	—	—	—	—	—	—
$BaBr_2$	0.517	0.469	0.450	0.438	0.446	0.473	(0.552)	0.661	(0.878)	(1.254)	—	—
BaI_2	0.536	0.503	0.496	0.517	0.556	0.642	(0.86)	1.208	(1.791)	(2.72)	(6.97)	(20.0)
$CaBr_2$	0.532	0.492	0.481	0.490	0.521	0.596	(0.81)	1.119	1.654	2.53	6.27	18.43
CaI_2	0.552	0.524	0.524	0.553	0.605	0.731	(1.01)	1.617	(2.468)	(3.973)	(11.63)	(42.3)
$Ca(NO_3)_2$	0.488	0.429	0.397	0.365	0.349	0.338	0.338	0.347	0.362	0.382	0.438	0.510
$Cd(NO_3)_2$	0.516	0.467	0.445	0.428	0.426	0.436	(0.48)	0.518	0.573	(0.630)	(0.764)	(0.919)
$CdSO_4$	0.150	0.102	0.0829	0.0615	0.0505	0.0415	0.0342	0.0321	0.0317	0.0329	—	—
$CoCl_2$	0.523	0.479	0.463	0.462	0.479	0.531	(0.685)	0.860	1.120	1.458	2.22	—
$Co(NO_3)_2$	0.540	0.474	0.465	0.448	0.458	0.493	(0.585)	0.730	0.926	1.189	1.984	3.33
CsBr	0.754	0.694	0.654	0.603	0.571	0.538	0.505	0.486	0.474	0.465	0.457	0.453
$CsCH_3COO$	0.799	0.771	0.761	0.762	0.776	0.802	0.868	0.950	1.041	1.145	(1.397)	(1.689)
CsCl	0.756	0.694	0.656	0.606	0.575	0.544	0.514	0.496	0.485	0.479	0.474	0.475
CsI	0.754	0.692	0.651	0.599	0.567	0.533	0.495	0.470	0.450	0.434	—	—
$CsNO_3$	0.733	0.655	0.602	0.528	0.478	0.422	—	—	—	—	—	—
CsOH	0.809	0.774	0.757	0.752	0.761	0.785	—	—	—	—	—	—
Cs_2SO_4	0.464	0.390	0.345	0.297	0.267	0.240	0.215	(0.200)	(0.191)	(0.184)	(0.177)	(0.173)
$CuCl_2$	0.510	0.457	0.431	0.413	0.411	0.419	(0.434)	0.463	0.496	0.522	0.575	0.623
$Cu(NO_3)_2$	0.512	0.461	0.440	0.427	0.432	0.456	(0.528)	0.610	0.728	0.905	1.384	2.05
$CuSO_4$	0.150	0.104	0.0829	0.0620	0.0512	0.0423	—	—	—	—	—	—
$FeCl_2$	0.520	0.475	0.456	0.452	0.465	0.509	(0.640)	0.790	0.923	1.215	1.773	2.479
$HClO_4$	0.803	0.778	0.768	0.769	0.785	0.823	0.923	1.055	1.227	1.448	2.08	3.11
HI	0.818	0.807	0.811	0.839	0.883	0.965	1.139	1.356	1.641	2.015	(3.122)	(5.06)
$KBrO_3$	0.745	0.674	0.625	0.552	—	—	—	—	—	—	—	—

Appendix 10 (concluded)

Electrolyte	γ at m =											
	0.1	0.2	0.3	0.5	0.7	1.0	1.5	2.0	2.5	3	4	5
KCH_3COO	0.796	0.766	0.754	0.751	0.759	0.783	0.840	0.910	0.995	1.086	(1.284)	(1.503)
KCNS	0.769	0.716	0.685	0.646	0.623	0.599	0.573	0.556	0.546	0.538	0.529	0.524
$KClO_3$	0.749	0.681	0.635	0.568	0.518	—	—	—	—	—	—	—
KF	0.775	0.727	0.700	0.670	0.654	0.645	0.646	0.658	0.678	0.705	0.779	0.874
KH_2PO_4	0.731	0.653	0.602	0.529	0.477	0.421	0.359	—	—	—	—	—
KNO_3	0.739	0.663	0.614	0.545	0.496	0.443	0.380	0.333	0.297	0.269	—	—
K_2CrO_4	0.466	0.390	0.347	0.298	0.269	0.240	0.215	0.200	0.194	0.194	—	—
K_2SO_4	0.436	0.356	0.313	0.261	0.229	—	—	—	—	—	—	—
LiBr	0.796	0.766	0.756	0.753	0.767	0.803	0.896	1.015	1.16	1.341	1.897	2.74
$LiCH_3COO$	0.784	0.742	0.721	0.700	0.689	0.689	0.705	0.729	0.762	0.798	0.877	(0.964)
LiCl	0.790	0.757	0.744	0.739	0.748	0.774	0.838	0.921	1.026	1.156	1.510	2.02
$LiClO_4$	0.812	0.794	0.792	0.808	0.834	0.887	(0.995)	1.158	1.350	1.582	2.18	(2.98)
LiI	0.815	0.802	0.804	0.824	0.852	0.910	1.03	1.198	1.418	1.715	(2.536)	(3.87)
$LiNO_3$	0.788	0.752	0.736	0.726	0.729	0.743	0.783	0.835	0.896	0.966	1.125	1.310
LiOH	0.718	0.663	0.628	0.583	0.553	0.529	0.500	0.485	0.475	0.467	0.454	0.456
Li_2SO_4	0.478	0.406	0.369	0.326	0.303	0.283	0.270	0.269	—	—	—	—
$MgBr_2$	0.542	0.512	0.511	0.538	0.591	0.714	(1.04)	1.593	2.56	4.20	12.2	36.1
$MgCl_2$	0.528	0.488	0.476	0.480	0.505	0.569	(0.775)	1.051	1.538	2.32	5.53	13.92
$Mg(ClO_4)_2$	0.577	0.565	0.576	0.633	0.723	0.925	(1.51)	2.59	4.78	8.99	33.3	—
MgI_2	0.571	0.550	0.558	0.605	0.688	0.879	(1.41)	2.39	4.27	7.81	28.6	113
$Mg(NO_3)_2$	0.522	0.480	0.467	0.469	0.488	0.536	(0.66)	0.835	—	—	—	—
$MnCl_2$	0.518	0.471	0.452	0.442	0.450	0.481	(0.571)	0.671	0.796	0.938	1.240	1.56

$MnSO_4$	0.150	0.105	0.0848	0.0640	0.0530	0.0439	0.0373	0.0351	0.0349	0.0373	0.0473	—
$NaBrO_3$	0.758	0.696	0.657	0.605	0.569	0.528	(0.481)	0.450	0.426	—	—	—
$NaCH_3COO$	0.791	0.757	0.744	0.735	0.740	0.757	0.799	0.851	0.914	0.982	(1.132)	(1.297)
NaCNS	0.787	0.750	0.731	0.715	0.710	0.712	0.727	0.744	0.779	0.814	0.897	1.009
$NaClO_3$	0.772	0.720	0.688	0.645	0.617	0.589	(0.558)	0.538	0.525	0.515	0.500	0.488
$NaClO_4$	0.775	0.729	0.701	0.668	0.648	0.629	(0.614)	0.609	0.609	0.611	0.626	0.649
NaF	0.765	0.710	0.676	0.632	0.603	0.573	—	—	—	—	—	—
NaI	0.787	0.751	0.735	0.723	0.724	0.736	0.771	0.820	0.883	0.978	1.25	1.72
NaH_2PO_4	0.744	0.675	0.629	0.563	0.517	0.468	(0.410)	0.371	0.343	0.320	0.293	0.276
Na_2CrO_4	0.479	0.407	0.364	0.317	0.289	0.261	0.237	0.229	0.232	0.244	0.294	(0.410)
$Na_2S_2O_3$	0.466	0.390	0.347	0.298	0.267	0.239	0.214	0.202	0.199	0.203	(0.222)	—
$NiCl_2$	0.523	0.479	0.463	0.464	0.482	0.536	(0.70)	0.906	1.236	1.692	2.96	4.69
$NiSO_4$	0.150	0.105	0.0848	0.0627	0.0515	0.0425	0.0360	0.0343	0.0357	—	—	—
RbBr	0.763	0.706	0.673	0.632	0.605	0.578	0.552	0.536	0.526	0.520	0.514	0.515
$RbCH_3COO$	0.796	0.767	0.756	0.755	0.766	0.792	0.856	0.933	1.023	1.126	(1.365)	(1.644)
RbCl	0.764	0.709	0.675	0.634	0.607	0.583	0.559	0.546	0.539	0.536	0.538	0.543
RbI	0.762	0.705	0.671	0.629	0.602	0.575	0.548	0.533	0.524	0.518	0.515	0.517
$RbNO_3$	0,734	0.658	0.606	0.534	0.485	0.430	0.366	0.321	0.285	0.257	0.216	—
Rb_2SO_4	0.460	0.382	0.338	0.285	0.234	0.224	0.197	—	—	—	—	—
$SrBr_2$	0.527	0.483	0.468	0.467	0.484	0.535	(0.68)	0.906	(1.269)	(1.791)	(3.897)	—
$SrCl_2$	0.515	0.466	0.446	0.437	0.437	0.465	(0.55)	0.675	0.862	1.135	1.993	—
SrI_2	0.549	0.516	0.513	0.532	0.573	0.675	(0.90)	1.396	(2.12)	(3.31)	(9.01)	(28.14)
$Sr(NO_3)_2$	0.478	0.410	0.373	0.329	0.302	0.283	(0.258)	0.238	0.232	0.223	0.214	—
$Th(NO_3)_4$	0.279	0.225	0.203	0.189	0.191	0.207	(0.262)	0.326	0.405	0.486	0.647	0.791
$TlCH_3COO$	0.750	0.686	0.644	0.589	0.553	0.515	0.472	0.444	0.422	0.405	0.376	0.354
$Zn(ClO_4)_2$	0.581	0.564	0.573	0.629	0.720	0.929	(1.5)	2.74	5.15	9.99	38.8	—
$Zn(NO_3)_2$	0.530	0.487	0.472	0.471	0.487	0.533	(0.650)	0.814	1.045	1.358	2.30	3.86

APPENDIX 11

GROUP COEFFICIENTS AND CORRECTIONS FOR DEVIATION IN STRUCTURE OF HYDROCARBON NEEDED TO CALCULATE $(\Delta G^{\circ}_{T})_{form}$ (IN KCAL/MOL) ACCORDING TO D. VAN KREVELEN AND H. CHERMIN *

A. Group Coefficients of Eq. (13.15) for Alkanes, Naphthenes, Alkenes, Alkynes and Aromatic Hydrocarbons

Group	T = 300-600		T = 600-1500	
	a	$b \times 10^2$	a	$b \times 10^2$
CH_4	−18.719	2.180	−21.161	2.587
$-CH_3$	−10.833	2.176	−12.393	2.436
$>CH_2$	−5.283	2.443	−5.913	2.548
$>CH$	−0.756	2.942	−0.756	2.942
$>C<$	3.060	3.636	3.840	3.506
$H_2C=CH_2$	11.653	1.552	9.451	1.889
$H_2C=C<_{H}$	14.281	1.642	13.513	1.770
$H_2C=C<$	16.823	1.864	15.785	2.037
$H-C=C-H$ (*cis*)	18.407	1.834	16.781	2.114
$H-C=C-H$ (*trans*)	17.019	2.007	16.755	2.051
$H-C=C<$	20.273	2.306	19.913	2.366
$>C=C<$	23.955	2.839	25.731	2.543
$H_2C=C=CH_2$	45.293	1.010	43.439	1.319
$H_2C=C=C<_{H}$	48.871	1.063	48.133	1.186
$H_2C=C=C<$	51.159	1.481	51.159	1.481
$H-C=C=C<$	53.176	1.528	52.690	1.609
$HC\equiv$	27.104	−0.775	26.678	−0.704

* Van Krevelen, D. W. and Chermin, H. A. *Chem. Eng. Sci.* 1 : 66 (1951), 1 : 238 (1952); Chermin, H. A. *Petr. Ref.* **40**, 2 : 145 (1961).

Appendix 11 (continued)

Group	T = 300-600		T = 600-1500	
	a	$b \times 10^2$	a	$b \times 10^2$
$-C\equiv$	27.478	−0.617	27.346	−0.595
HC< (aromatic)	3.100	0.610	2.536	0.704
−C< (ditto)	5.280	0.994	5.634	0.935
←C<	2.260	0.553	2.566	0.502
Conjugated alkenes :				
$H_2C\leftrightarrow$	9.634	1.088	8.980	1.197
HC<	3.100	0.610	2.536	0.704
HC<	12.302	1.438	12.408	1.420
←C<	5.280	0.994	5.634	0.935

B. Coefficients of Corrections for Deviation in Structure of Alkanes, Naphthenes and Aromatic Hydrocarbons

Correction	T = 300-600		T = 600-1500	
	a	$b \times 10^2$	a	$b \times 10^2$
Branching in alkanes :				
side chain with 2C and more	1.31	0.0	1.31	0.0
3 adjacent HC<	2.312	0.0	2.312	0.0
adjacent >CH and >C<	1.625	0.0	1.625	0.0
2 adjacent >C<	2.543	0.0	2.543	0.0
Formation of naphthene rings :				
three-membered	27.215	−3.147	26.495	−3.027
four-membered	25.689	−2.901	24.459	−2.696
five-membered	5.511	−2.583	3.417	−2.234
six-membered	−0.707	−1.623	−1.145	−1.550
cyclopentene	3.455	−2.448	2.189	−2.237
cyclohexene	−1.043	−2.070	−0.737	−2.121

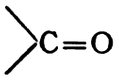
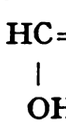
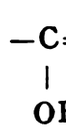
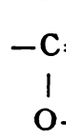
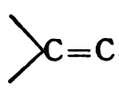
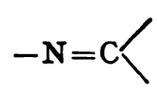
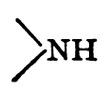
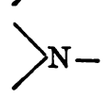
Appendix 11 (continued)

Correction	T = 300-600		T = 600-1500	
	a	$b \times 10^2$	a	$b \times 10^2$
Branching in naphthenes:				
five-membered ring				
one group	−0.665	−0.065	−0.443	−0.102
two groups in position 1,1	−1.880	−0.138	−1.112	−0.266
cis 1,2	−1.485	0.245	0.939	−0.159
trans 1,2	−2.163	−0.138	−1.377	−0.269
cis 1,3	−1.423	0.0	−0.637	−0.131
trans 1,3	−1.888	−0.138	−1.048	−0.278
six-membered ring				
one group	−0.370	−0.106	0.452	−0.243
two groups in position 1,1	−1.722	0.0	−0.432	−0.215
cis 1,2	−0.500	0.0	1.432	−0.322
trans 1,2	−2.003	−0.138	−0.173	−0.443
cis 1,3	−3.055	0.0	−1.687	−0.228
trans 1,3	−1.718	0.0	0.262	−0.330
cis 1,4	−1.152	0.0	0.0	−0.192
trans 1,4	−3.125	0.034	−1.205	−0.286
Branching in aromatic rings:				
position 1,2	0.955	0.055	1.687	−0.067
1,3	0.352	−0.057	0.574	−0.094
1,4	−0.183	0.105	0.615	−0.028
1,2,3	1.453	−0.112	1.039	−0.043
1,2,4	0.297	−0.070	0.243	−0.061
1,3,5	−0.320	−0.137	−0.436	−0.116
1,2,3,4	3.664	−0.007	4.456	−0.139
1,2,3,5	2.861	0.025	3.359	−0.058
1,2,4,5	2.736	−0.150	3.072	−0.206
5 substitutions	4.400	0.091	5.468	−0.087
6 substitutions	8.254	0.260	10.006	−0.032

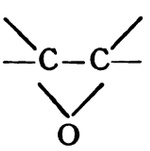
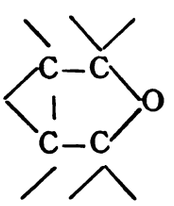
C. Group Coefficients for Non-Carbon Groups

Group	T = 300-600		T = 600-1500	
	a	$b \times 10^2$	a	$b \times 10^2$
H_2O	−58.076	1.154	−59.138	1.316
—O—	−15.790	−0.85	—	—

Appendix 11 (continued)

Group	T = 300-600		T = 600-1500	
	a	$b \times 10^2$	a	$b \times 10^2$
	−18.37	0.80	−16.07	0.40
H_2CO	−29.118	0.653	−30.327	0.854
	−29.16	0.663	−30.102	0.802
	−28.08	0.91	−28.08	0.91
	−87.66	2.473	−90.569	2.958
	−98.39	2.86	−98.83	2.93
	−92.62	2.61	−92.62	2.61
$H_2C=CO$	−14.515	0.295	−14.515	0.295
	−12.86	0.46	−12.86	0.46
	−9.62	0.72	−9.38	0.73
HCN	31.179	−0.826	30.874	−0.775
$-C\equiv N$	30.75	−0.72	30.75	−0.72
	46.32	−0.89	46.32	−0.89
NH_3	−11.606	2.556	−12.972	2.784
$-NH_2$	2.82	2.71	−6.78	3.98
	12.93	3.16	12.93	3.16
	19.46	3.82	19.46	3.82
	11.32	1.11	12.26	0.96
$-NO_2$	−9.0	3.70	−14.19	4.38
HF	−64.476	−0.145	−64.884	−0.081
F−	−45.10	−0.20	—	—
HCl	−22.10	−0.215	−22.460	−0.156

Appendix 11 (concluded)

Group	T = 300-600		T = 600-1500	
	a	$b \times 10^2$	a	$b \times 10^2$
—Cl	—8.25	0.0	—8.25	0.0
HBr	—12.533	—0.234	—13.010	—0.158
—Br	—1.62	—0.26	—1.62	—0.26
HI	—1.130	—2.215	—1.718	—0.176
—I	7.80	0.0	7.80	0.0
H_2S	—20.552	1.026	—21.366	1.167
—S—	—3.32	1.42	—3.32	1.44
	—0.97	0.51	—0.65	0.44
—S—S—	—18.606	2.664	—18.204	2.597
—SH (primary)	—11.827	0.975	—11.815	0.973
=SO	—30.19	3.39	—30.19	3.39
$=SO_2$	—82.58	5.58	—80.69	5.26
—OH (primary)	—42.959	1.134	—43.103	1.158
—OH (secondary)	—44.538	1.18	—44.232	1.136
—OH (tertiary)	—49.407	1.020	—49.193	1.001
—OH (aryl)	—45.644	1.533	—45.506	1.510
Rings :				
	12.86	—0.63	12.86	—0.63
	—5.82	0.25	—3.53	—0.16

APPENDIX 12

VALUES OF FUNDAMENTAL PHYSICAL CONSTANTS AND RELATIONSHIPS BETWEEN SELECTED QUANTITIES

Quantity	CGS and non-system units	SI (MKSA) units
Avogadro constant, N_A	$(6.022\,045 \pm 0.000\,031) \times 10^{23}$ mol^{-1}	$(6.022\,045 \pm 0.000\,031) \times 10^{23}$ mol^{-1}
Volume of ideal gas in standard conditions at 0 °C	22 413.6 cm^3/mol 22.4136 dm^3/mol	22.4136×10^{-3} m^3/mol
Thermochemical calorie, cal	$4.184\,00 \times 10^7$ erg	4.184 00 J
Atmosphere (physical), atm	1 013 250 dyn/cm^2 760 mm Hg	101 325 N/m^2
Bar	1×10^6 dyn/cm^2	1×10^5 N/m^2
Torr	1 mm Hg	133.322 Pa
Molar gas constant, R	$(8.314\,41 \pm 0.000\,26) \times 10^7$ erg/mol · K (1.987 17 + 0.000 08) cal/mol · K (82.0556 + 0.0035) cm^3 · atm/mol · K	(8.314 41 ± 0.000 26) J/mol · K
Boltzmann constant $k = R/N_A$	$(1.380\,662 \pm 0.000\,044) \times 10^{-16}$ erg/K	$(1.380\,662 \pm 0.000\,044) \times 10^{-23}$ J/K
Planck constant, h	$(6.626\,176 \pm 0.000\,036) \times 10^{-27}$ erg/s	$(6.626\,176 \pm 0.000\,036) \times 10^{-34}$ J · s
Charge of electron, e	$(1.602\,189\,2 \pm 0.000\,004\,6) \times 10^{-20}$ emu $(4.802\,98 \pm 0.000\,07) \times 10^{-10}$ esu	$(1.602\,189\,2 \pm 0.000\,004\,6) \times 10^{-19}$ C
Faraday constant, F	$(9.648\,456 \pm 0.000\,027) \times 10^4$ C/g-eq	$(9.648\,456 \pm 0.000\,027) \times 10^4$ C/mol
$R \ln x$	$(19.144\,47 \pm 0.000\,82) \times 10^7 \log x$ erg/mol · K $(4.575\,63 \pm 0.000\,19) \times \log x$ cal/mol · K	$(19.144\,47 \pm 0.000\,82) \times \log x$ J/mol · K

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